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Some minerals from the leucite-rich rocks of the West Kimberley area, Western Australia.

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In the investigation of a suite of leucite-lamproites from the West Kimberley area of Western Australia, carried out in the Department of Mineralogy and Petrology, Cambridge, during the period 1937–38, a number of unusual minerals were noted. Three of these were isolated and analysed and two of them proved to be new species. The present paper deals mainly with the three minerals analysed. They are—

(1) Magnophorite, a new amphibole allied to katophorite.
(2) Wadeite, a new potassium-zirconium silicate.
(3) Titaniferous phlogopite.

Field occurrence.

The leucite-bearing rocks occur at a number of isolated volcanic vents, nineteen of which have been examined and mapped by Dr. A. Wade. They have in every instance broken through sedimentary deposits of Permian age. Considerable diversity is to be seen in the rock types developed, but they are all characterized by high potash, magnesia, and titania, with low alumina and soda. Analyses of some types which illustrate the general chemical character of these rocks are given in table I. The minerals noted in this suite of rocks were leucite, phlogopite, diopside, katophoritic amphibole, rutile, and (?) nontronite (pseudomorphous after olivine), with wadeite, perovskite, and apatite as minor accessories, and serpentine, calcite, baryte, chalcedony, and various zeolites as secondary minerals and amygdales. A full account of the petrography and petrogenesis of this very unusual suite of rocks will be

published shortly (Wade and Prider, 1939). In the present paper the unusual minerals mentioned above will be described.

TABLE I. Chemical analyses of some leucite-lamproites from the West Kimberley area, Western Australia.

	I.	II.	III.
SiO_2	45·82	52·45	54·48
TiO_2	7·34	5·85	5·57
Al_2O_3	6·86	8·64	9·87
Fe_2O_3	6·07	5·48	4·89
FeO	1·98	0·94	1·70
MnO	0·10	0·13	0·09
MgO	10·90	6·42	5·35
CaO	4·70	2·01	1·89
Na_2O	0·84	0·38	0·88
K_2O	8·82	10·42	11·06
H_2O+	0·75	1·99	1·36
H_2O-	2·40	2·89	0·89
CO_2	0·08	nil	nil
P_2O_5	1·83	1·58	0·40
BaO	1·27	1·19	0·64
SrO	n.d.	n.d.	0·16
ZrO_2	n.d.	n.d.	0·07
SO_3	n.d.	nil	0·10
FeS_2	0·07	n.d.	0·20
Cr_2O_3	0·07	n.d.	trace
V_2O_3	0·03	n.d.	n.d.
F	present	n.d.	0·09
	99·93	100·37	99·69
Less O= F ...	—	—	0·04
			99·65

I. Diopside-phlogopite-magnophorite-leucite-lamproite. Analyst, C. R. Le Mesurier.

II. Phlogopite-leucite-lamproite. Analyst, D. G. Murray (E. S. Simpson, 1926, p. 59.).

III. Magnophorite-leucite-lamproite. Analyst, R. T. Prider.

Magnophorite, a new amphibole allied to katophorite.

This mineral occurs as an essential and abundant constituent of most of the lamproites examined. It has invariably been the last essential mineral to separate and usually has a poikilitic structure enclosing euhedra of leucite and diopside (fig. 1). In one specimen from the Wolgidee Hills locality the amphibole is comparatively free from inclusions, except for calcite which frequently occurs as a coating on the cleavages. In this specimen the amphibole is idiomorphic towards a carbonated serpentinous groundmass and the forms developed are (110) and (010). The characteristic amphibole cleavages are well developed

By fine crushing, treatment in acetic acid, and centrifuging in heavy liquids, followed by a separation with the electromagnet, it was possible to obtain a pure product for analysis. The analysis together with the calculation of the structural formula on a basis of 24(O,OH,F) (Warren, 1930, p. 493) appears in table II.

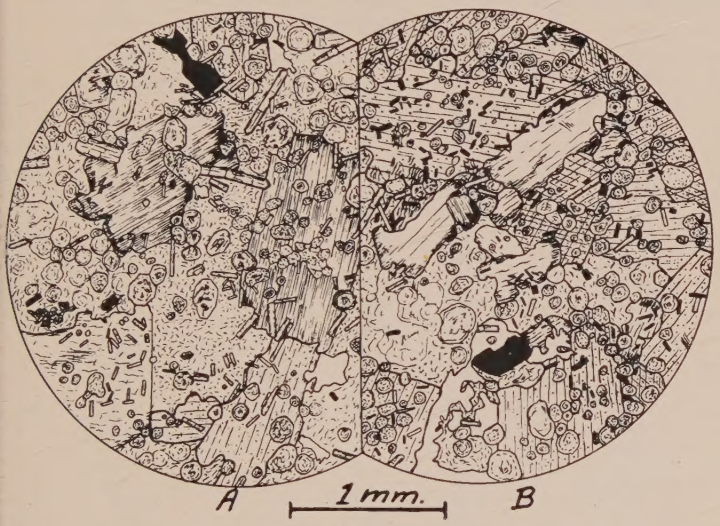

Fig. 1a. Lamproite (specimen no. 116a) from Moulamen Hill. Showing poikilitic inclusions of diopside and leucite in katophoritic amphibole (good prismatic cleavage; dotted) and phlogopite, the latter showing a dark resorption border. In lower left a well-shaped phlogopite plate is somewhat corroded. The groundmass is mainly greenish serpentine. Rutile as opaque rods and prisms.

Fig. 1b. Lamproite (specimen no. 456a) from Mt. North. Showing phlogopite (with dark resorption border) free from inclusions, and katophoritic amphibole (forming the greater part of the field) with poikilitic inclusions of diopside, leucite, and rutile. The groundmass is of serpentine. Irregular clear skeletal areas of zeolite.

The characteristics of this mineral are:

Specific gravity 3·12. Colour, pale reddish-brown.

Pleochroism: α colourless to pale yellow; β reddish, like α in hypersthene and increasing rapidly in intensity with increasing thickness; γ pale to bright yellow, occasionally slightly greenish. Absorption $\beta > \gamma > \alpha$.

Optic axial plane (010), $\beta = b$, $\gamma : c = 26°$, 2V 70°. Dispersion rather strong, $r < v$.

Refractive indices: α 1·616, γ 1·632, $\gamma - \alpha$ 0·016.

The absorption and pleochroism are indicative of a member of the katophorite group, but the analysis shows that the FeO and Fe_2O_3 of the normal katophorite have been replaced almost entirely by MgO. Another notable feature of this amphibole is the marked dominance of

TABLE II. Chemical analysis and calculation of katophoritic amphibole from specimen no. 242a, Wolgidee Hills, West Kimberley, Western Australia.

Analyst, H. C. G. Vincent.

	Wt. %	Molecular proportions.	No. of metal atoms on basis of 24(O,OH,F).		
SiO_2 ...	52·67	0·878	7·582		
Al_2O_3 ...	1·72	0·017	0·294		8·000
TiO_2 ...	3·53	0·044	0·380	0·124	
				0·256	
Fe_2O_3 ...	0·58	0·004	0·069		
FeO ...	2·41	0·033	0·285		5·222
MnO ...	0·06	0·001	0·009		
MgO ...	21·32	0·533	4·603		
CaO ...	6·95	0·124	1·071		
SrO ...	0·15	0·001	0·009		
BaO ...	nil	—	—	...	3·152
Na_2O ...	3·64	0·059	1·019		
K_2O ...	5·70	0·061	1·053		
Li_2O ...	n.d.	—	—		
ZrO_2 ...	nil	—	—		
H_2O- ...	nil	—	—		
H_2O+ ...	0·46	0·026	0·449	...	1·036
F ...	1·29	0·034	0·587		
	100·48				
Less O = F	0·54				
	99·94				

K_2O over Na_2O. The above calculation in table II shows that the structural formula of the mineral is:

$$(OH,F)_{1\cdot04}\ (Ca,Na,K)_{3\cdot15}\ (Mg,Fe,Ti,Mn)_{5\cdot22}\ (Si,Al,Ti)_{8\cdot00}O_{22}.$$

This agrees fairly well with the typical amphibole structural formula, the main points of difference being the low value of 1·04 for (OH,F) and the high value of 3·15 for (Ca,Na,K).

In table III are set down the analyses and optical properties of various amphiboles which show some affinities to that described above. From this table it will be seen that, optically, the Western Australian amphibole appears to be a katophorite; chemically, however, the closest relatives are imerinite, szechenyiite, and richterite. The two former amphiboles differ from the Western Australian mineral in having a considerable Na_2O content and very little K_2O. Richterite, the manganese-rich

metamorphic amphibole, differs only in having a considerable amount of MnO and no TiO_2. The normal katophorite and anophorite have a high iron content, which in the Western Australian mineral has been replaced

TABLE III. Chemical analyses and optical data of various alkalic amphiboles showing affinities to the Western Australian amphibole.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
SiO_2	52·67	46·87	41·53	53·73	55·02	49·79	55·64	54·15
TiO_2	3·53	1·03	1·12	0·41	—	5·37	nil	—
Al_2O_3	1·72	7·97	10·27	2·72	4·53	1·98	1·08	0·52
Fe_2O_3	0·58	5·52	25·02	4·72	1·04	7·54	—	1·77
FeO	2·41	8·57		4·70	3·28	9·18	6·35	2·80
MnO	0·06	1·18	—	—	—	0·36	0·77	5·09
MgO	21·32	13·22	6·32	20·60	20·36	11·59	22·09	20·18
CaO	6·95	7·69	9·34	2·73	8·00	3·16	7·64	6·06
SrO	0·15	—	—	—	—	trace	—	—
BaO	nil	—	—		—	—	nil	—
Na_2O	3·64	4·46	3·62	7·42	6·71	7·92	2·89	2·77
K_2O	5·70	1·75	1·21	1·82	1·52	1·85	0·98	6·37
H_2O+	0·46	1·87	1·65	0·85	0·51	1·52	2·95	0·12
F ...	1·29	—	—	0·92	—	—	nil	—
	100·48	'100·33'	100·08	100·62	100·97	100·26	100·39	99·83
Sp. gr.	3·12	3·201	3·408	3·02	3·033	3·166	3·0	—
α	1·616	1·655	—	—	—	—	—	—
γ	1·632	1·662	—	—	—	—	—	—
$\gamma-\alpha$	0·016	0·007	—	—	—	—	0·020–0·030	—
Extinction	$\gamma : c$ 26°	$\alpha : c$ 56°	$\alpha : c$ 66°	$\gamma : c$ 50°	16°16′	$\beta : c$ 20–28°	$\alpha : c$ 16–70°	—
2V	70°	small	—	small	—	2E 33–40°	—	—
Dispersion	strong $r < v$	—	—	strong	—	strong $r > v$	—	—

Pleochroism.

	α	β	γ	Absorption.
I.	pale yellow	reddish	yellow	$\beta > \gamma > \alpha$
III.	clear green	brownish-red	reddish-yellow	$\beta > \gamma > \alpha$
IV.	pale yellowish-green	bluish-violet	pale bluish-green	$\beta > \gamma = \alpha$
VI.	pale yellow	greenish	reddish-brown	$\gamma > \beta < \alpha$
VII.	pinkish-lilac	paler lilac	blue	—

I. Amphibole from lamproite specimen no. 242a, Wolgidee Hills, West Kimberley area, Western Australia.

II. Katophorite, Khibina, Kola Peninsula, Russia. (Kunitz, 1930, pp. 219, 245.)

III. Katophorite, Grouvsletten, Norway. (Kunitz, 1930, pp. 219, 245.)

IV. Imerinite, Madagascar. (Lacroix, 1910, p. 787; 1922, p. 538.)

V. Szechenyiite, Burma. (Krenner, 1899, p. 503.)

VI. Anophorite, Katzenbuckel, Odenwald, Germany. (Freudenberg, 1908, p. 76; Rosenbusch, 1910, p. 201.)

VII. Winchite, Jhabua State, Central India. (Fermor, 1909, p. 149.)

VIII. Richterite, Långban, Sweden. (Magnusson, 1930, p. 45.)

almost entirely by MgO. Also the katophorite has much of its SiO_2 replaced by Al_2O_3. The alkalis in the Western Australian mineral differ considerably from those of katophorite and anophorite, which both have soda dominant over potash. The richterite from Långban is the only amphibole in the above table which has a similar content and relative proportion of soda and potash to the Western Australian mineral.

This mineral is therefore best described as a kali-magnesio-katophorite, and as it differs considerably from the normal katophorite in chemical composition it appears to warrant a new name. In an earlier summary report (Wade and Prider, 1938; Prider, 1939) on these leucite-rocks the name simpsonite was proposed for this mineral. Almost simultaneously the name simpsonite was proposed by H. Bowley for a new hydrous tantalate of calcium and aluminium from Tabba Tabba, Western Australia (Bowley, 1938, 1939), so the name *magnophorite* is now suggested for this mineral.

From the analyses of the leucite-rocks which contain magnophorite (analyses I and III in table I) it will be seen that this mineral, which has been invariably the last to crystallize, has separated from a residuum (after crystallization of the earlier phlogopite, diopside, and leucite) which was rich in potash, magnesia, titania, and silica, and which contained very little alumina.

A similar mineral to the above has been recorded from two localities. Osann (1906, p. 295) has described an amphibole with similar pleochroism and absorption from the jumillites of Murcia, Spain, and Cross (1897, p. 125) records the presence of a similar amphibole in the rock orendite from the Leucite Hills, Wyoming. In both instances the mineral was considered to be katophorite, but in neither case was the mineral examined chemically. With regard to the amphibole occurring in the orendite of the Leucite Hills, Cross (1897, p. 126) states: extinction seems to be always parallel to the length axis; $\alpha = a$, pale yellow; $\beta = b$, red similar to hypersthene; $\gamma = c$, bright yellow; absorption $\beta > \gamma > \alpha$; almost uniaxial with the arms barely separating in the 45° position.

An examination of the amphibole in the orendite specimen in the Petrology Museum at Cambridge shows that this mineral is often zoned, with extinction-angles $\gamma : c = 5°$ for the periphery and 17° for the centre. Extinction is rarely straight (as stated by Cross) and frequently is as much as 25°. The mineral has the same pleochroism, absorption, and strong dispersion as noted in the mineral described above as magnophorite, but has slightly higher refringence, β measured on several minute prisms being 1·643. This mineral, therefore, is essentially the

ame as magnophorite. Its paragenesis is the same as for the Western ustralian mineral, as it is associated with diopside, phlogopite, and ucite, and has separated from a potash-silica-rich and alumina-poor esiduum after the formation of diopside, phlogopite, and leucite.

Cross (1897, p. 131) suggests, in view of the considerable zirconia ontent (0·22 %) of the orendites, 'that the peculiar amphibole of orendite perhaps zirconia-bearing, analogous to låvenite, wöhlerite, and hiort-ahlite'. Acting on this suggestion I determined zirconia on a slightly mpure sample of magnophorite (containing not more than 5% impurity) nd found this constituent to be absent.

Wadeite, a new potassium-zirconium silicate.

This new mineral was found in the rocks from the Wolgidee Hills, and mongst all the specimens examined it has only been noted from this ocality. The material analysed was pparated from the same specimen as he magnophorite described above, iz. no. 242a. In this rock the wadeite present to the extent of about 1 or %, occurring as highly birefringent risms up to 1 mm. in length and as exagonal-shaped basal sections. It as crystallized before the magno-horite and is invariably idiomorphic owards it, but its relations with the iopside are not visible in any of my ices. It is invariably replaced in art (especially along the poor pyra-idal cleavages) by calcite.

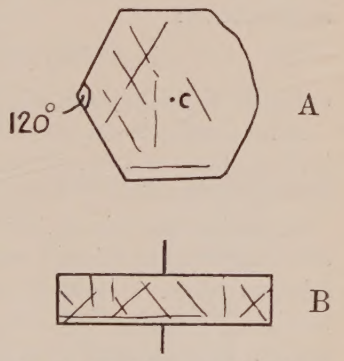

Fig. 2. Wadeite, showing forms developed.

A. Basal section showing imperfect (?) prism cleavages.

B. Section parallel to the *c*-axis, showing poor pyramidal cleavages intersecting at approximately 90°. A poor basal and prismatic cleavage also present.

It appears to be hexagonal and is sually as well-shaped crystals flattened n the base, the sections then appearing o have elongation of a negative char-cter. The faces developed are the base, rism, and occasionally a pyramid. Poor pyramidal cleavages intersecting t angles of nearly 90° are present in some crystals and are rendered isible because of the presence of secondary calcite which has entered along hese directions. Typical sections of the mineral are shown in fig. 2.

The mineral is colourless, uniaxial, optically positive, and has ϵ 1·655, 1·625, $\epsilon-\omega$ 0·030.

It has a specific gravity of 3·10, is non-magnetic and insoluble in hot acids.

The mineral was separated by centrifuging the fine-powdered, acid-treated rock in heavy liquids and later purified by separation with the electromagnet and finally by hand-picking. In all, only 0·5 gram was obtained and that included slight impurity (estimated at less than 5%). The analysis must therefore be regarded as correct only to the nearest whole number. Water above 110° C. was determined by loss on ignition on the main portion. The result of the analysis is shown in table IV. This table also shows the calculation of the analysis. In the third column the proportions of the groups of metal atoms has been worked out as shown and are found to be approximately:

$$(Si,P,Al):(Al,Ti,Mg,Zr):(Ca,Sr,Na):(K,Ba) = 4:1:1:2,$$

from which the formula (omitting the small amounts of Sr, Mg, and Ba) appears to be:

$$K_2(Ca,Na)\ (Zr,Ti,Al)\ (Si,P,Al)_4O_{12}(OH)$$

or ideally $K_2(Ca,Na)Zr(Si,Al)_4O_{12}(OH)$.

In the fourth column the number of metal atoms on a basis of 13(O,OH) is given, and it will be seen that the values obtained closely approach the ideal proportions of 4:1:1:2:1.

Regarding the 'loss on ignition' assumed in the above to be water above 110° C., the mineral was heated to redness and then examined microscopically. It suffered no apparent change during the heating, no signs of incipient fusion were present and the mineral retained its clarity. It is doubtful, therefore, whether any water is present in the structure of the mineral. The analysis has been recalculated on a basis of 12(O) and the 1·30% loss on ignition disregarded. The results of this calculation are shown in table V. The formula of the mineral according to this calculation is:

$$K_{2\cdot05}\ (Ca,Na)_{0\cdot95}(Zr,Ti,Al)_{1\cdot23}(Si,Al)_{4\cdot00}O_{12}.$$

Acting on the suggestion of Professor Tilley, attempts were made to synthesize the mineral. This work was conducted by Mr. H. C. G. Vincent to whom I am indebted for the following notes. An initial charge of K_2CO_3 1·382, $CaCO_3$ 1·001, ZrO_2 1·232, SiO_2 2·402 grams was heated for $\frac{3}{4}$ hour in the electric furnace to drive off the CO_2. After several attempts at heating in the Fletcher gas-furnace a pure glass was obtained. This was crushed and crystallized at a temperature of approximately 900° C. for 14 hours in the electric furnace, giving a crystalline

aass plus a little glass. Microscopical examination showed the crystals
o be in sheaf-like masses with negative elongation, straight extinction,
niaxial of positive optical character with a refractive index slightly

ABLE IV. Chemical analysis and calculation of wadeite. Analyst, R. T. Prider.

		Wt. %	Molecular proportions.	No. of metal atoms × 1000.		No. of metal atoms. on basis 13(O,OH).	
SiO_2	...	39·43	0·657	657		3·544	
P_2O_5	...	3·15	0·022	44	800	0·237	4·000
Al_2O_3	...	5·98	0·059	118 (99 + 19)		0·636 (0·417 + 0·219)	
$(Ce,Yt)_2O_3$	—	nil	—	—		—	
Fe_2O_3	...	trace	—	—		—	
TiO_2	...	1·63	0·020	20	219	0·108	1·298
MgO	...	0·28	0·007	7		0·038	
ZrO_2	...	21·29	0·173	173		0·933	
CaO	...	5·22	0·093	93		0·502	
SrO	...	0·16	0·002	2	... 185	0·011	... 0·998
Na_2O	...	2·82	0·045	90		0·485	
K_2O	...	18·40	0·196	392		2·114	
BaO	...	1·20	0·008	8	... 400	0·043	... 2·157
H_2O-	...	nil	—	—		—	
H_2O+	...	1·30	0·072	144	144	0·777	
		100·86					

ABLE V. Calculation of analysis of wadeite, assuming that no hydroxyl is present in the structure.

		Molecular proportions.	No. of oxygens.	No. of metal atoms on a basis of 12(O).		
SiO_2	...	0·657	1·314	3·372		
P_2O_5	...	0·022	0·110	0·226		4·000
Al_2O_3	...	0·059	0·177	0·605	(0·402 + 0·203)	
TiO_2	...	0·020	0·040	0·103		
MgO	...	0·007	0·007	0·036		1·230
ZrO_2	...	0·173	0·346	0·888		
CaO	...	0·093	0·093	0·477		
SrO	...	0·002	0·002	0·010	0·949	
Na_2O	...	0·045	0·045	0·462		3·002
K_2O	...	0·196	0·196	2·012	2·053	
BaO	...	0·008	0·008	0·041		
			2·338			

greater than 1·608. This material appeared to resemble pseudo-wollastonite, but it was insoluble in HCl. (Note: the natural mineral is similar n its optics to pseudo-wollastonite). These crystals must have had a omposition approaching $K_2CaZrSi_4O_{12}$, as there was very little glass left fter crystallizing for 14 hours: optically they are similar (but with omewhat lower refractive indices and different habit) to the natural

mineral. Another sample of the glass was now crystallized at 1300° C. (i.e. above the transition-point of pseudo-wollastonite) and the result was a colourless prismatic mineral (very similar to that obtained at 900° C.) plus some very highly refracting and highly birefringent rounded granules plus some glass.

A little of the natural mineral (slightly impure) was fused in a small platinum capsule in the Fletcher gas-furnace for ¾ hour. On quenching the melt the result was glass plus some very highly refringent granules (? similar to those obtained in crystallizing the artificial material at 1300° C.). The glass of the natural mineral melt was now crystallized at 1300° C. giving small prismatic crystals plus some glass.

The fusion experiment on the natural mineral appears to indicate that it melts incongruently to glass plus a very highly refringent material. Attempts at synthesizing the mineral gave at low temperatures of 900° C. a mineral very similar in optics but differing in habit. At higher temperatures of 1300° C. crystals plus highly refringent globules similar to those in the quenched melt of the natural mineral were obtained, thus supporting the suggestion that the natural mineral melts incongruently.

Returning to a consideration of the natural mineral, it is distinct from any previously described. Its closest relative is catapleiite from which it differs mainly in its low water and high potash content. The name proposed for this new mineral is *wadeite*, in honour of Dr. Arthur Wade, who was responsible for the collecting of this suite of rocks, and who discovered the new Wolgidee Hills intrusion where this mineral has been found.

Titaniferous Phlogopite.

This mineral occurs as a constant constituent of most of the leucite-bearing rocks. It appears to be fairly constant in character throughout the suite of rocks examined, except that in the more basic types it has a somewhat stronger absorption. One group of these rocks of widespread occurrence is made up entirely of this mineral plus leucite plus a very siliceous glassy groundmass. The phlogopite is usually phenocrystal, and the rocks appear to be surface flows as they usually show a flow orientation of the phlogopites or an elongation of the chalcedony-filled vesicles. The material for analysis was separated from an amygdaloidal phlogopite-leucite-lamproite from the Howe's Hill locality. The phlogopite in this rock is present as parallel alined, usually somewhat corroded, lath-shaped phenocrysts up to 2 mm. in length, which have crystallized earlier than the leucite and rutile which occurs as innumer-

le minute prisms in the glassy base. It is a deep reddish-brown colour, d is characterized by strong pleochroism after the scheme: α practi-ly colourless to pale salmon-pink, β bright yellow, γ reddish-brown. It has a comparatively large axial angle and always shows poly-nthetic twinning parallel to the base, which, owing to the marked fference in absorption along β and γ, is visible without the aid of the alyser, as the alternate lamellae show different pleochroism, one set lamellae from pale salmon-pink to bright yellow and the alternate nellae from pale salmon-pink to deep reddish-brown.

BLE VI. Chemical analysis and calculation of phlogopite from phlogopite-eucite-lamproite, Howe's Hill, Western Australia. Analyst, H. C. G. Vincent.

		Wt. %.	Molecular proportions.	No. of metal atoms on basis 12(O,OH,F).		
SiO_2	...	40·78	0·680	2·986		4·000
Al_2O_3	...	10·95	0·107	0·940		
TiO_2	...	8·97	0·113	0·496	0·074	
					0·422	2·925
Cr_2O_3	...	trace	—	—		
Fe_2O_3	...	2·18	0·014	0·123		
FeO	...	3·73	0·051	0·224		
MnO	...	trace	—	—		
MgO	...	19·66	0·491	2·156		
CaO	...	0·11	0·002	0·009		
SrO	...	trace	—	—		
BaO	...	0·35	0·002	0·009	...	1·028
Na_2O	...	0·11	0·002	0·018		
K_2O	...	10·59	0·113	0·992		
Li_2O	...	nil	—	—		
H_2O-	...	0·19	—	—		
H_2O+	...	1·87	0·106	0·931	...	1·080
F	...	0·66	0·017	0·149		
		100·15				
$-O = F$		0·27				
		99·88				

The analysis of this mineral is shown in table VI and the optical operties are:

Colour, deep reddish-brown.

Pleochroism: α pale salmon-pink to practically colourless, β bright yellow, γ reddish-brown. Absorption $\alpha<\beta<\gamma$.

α 1·599, γ 1·643, $\gamma-\alpha$ 0·044; $\alpha:c$ to 5°.

2V 38°, negative; dispersion very strong, $r<v$.

The structural formula (calculated in table VI):

$$(OH,F)_{1\cdot08}(Ca,Ba,Na,K)_{1\cdot03}(Mg,Fe'',Fe''',Ti)_{2\cdot92}(Si,Al,Ti)_{4\cdot00}O_{10}$$

agrees with the general structural formula for biotite with the exception of the (OH,F) group, which is very low in the above mineral. This appears to be a constant feature of the micas in these rocks. A determination of the water and fluorine content of a phlogopite separated from a similar rock from the Bruton's Hill locality gave H_2O 1·51, F 1·13%. The water was determined by the Penfield method in a silica tube, and in view of the fluorine present is, if anything, a little high.

It will be remembered that in the calculation of the structural formula for magnophorite it was found that the (OH,F) content was considerably lower than that required in the amphibole structure. This deficiency of (OH,F) in the two important hydroxyl-bearing minerals seems to be significant and to point to the deficiency as being due to (*a*) a loss of volatiles from these minerals during the period of intrusion of the rocks under low-pressure conditions at or near the surface, or (*b*) the separation of these minerals from an extremely 'dry' magma.

With regard to the possibility of loss of volatiles from these minerals during their crystallization at shallow depths, a possible clue is presented by the analysis of the phlogopite from the wyomingite of the Leucite Hills, Wyoming (table VII, analysis IV). This phlogopite is similar in occurrence and association to the Western Australian mineral and, with the exception of the high titania in the latter, these two analyses are very similar. The structural formula for the Wyoming phlogopite is:

$$(OH,F)_{2\cdot18}(Ca,Ba,Na,K)_{1\cdot06}(Mg,Fe'',Fe''',Ti)_{2\cdot67}(Si,Al,Ti)_{4\cdot00}O_{10}.$$

There is no deficiency here in the (OH,F) content. Also, an optically similar mica is noted in the jumillites of Spain, and although a complete analysis has not been made of this mineral, a determination of its fluorine content of 2·16% (Osann, 1906, p. 293) indicates that there has been little loss of volatiles. These two similar occurrences of phlogopite appear to indicate the improbability of loss of volatiles as the explanation of the very low hydroxyl-fluorine content of the Western Australian mineral.

A glance at table VII, in which are set down the analyses of other micas comparable in composition with that described above, shows that in the titania-rich types the hydroxyl content is low, as in the Western Australian phlogopite. Unfortunately fluorine has not been determined in either of these analyses. The mica from the Howe's Hill rock differs from that in wyomingite only in its high TiO_2, which has replaced some of the SiO_2, Al_2O_3, and MgO. Both of these micas show the same peculiar twinning and pleochroism, but the absorption of the Howe's Hill mica is much stronger than that of the Wyoming phlogopite and its refrin-

nce is much higher. (A determination on the phlogopite from the omingite in the Cambridge collection gave β 1·595).

In view of the very high TiO_2 content, together with the high MgO and O, the mica in the Western Australian leucite-rocks is best described a titaniferous phlogopite.

BLE VII. Micas comparable in composition with the West Kimberley phlogopite.

	I.	II.	III.	IV.
SiO_2 ...	40·78	37·47	36·12	42·56
Al_2O_3 ...	10·95	12·91	14·89	12·18
TiO_2 ...	8·97	10·86	7·68	2·09
Cr_2O_3 ...	trace	—	—	0·73
Fe_2O_3 ...	2·18	0·88	7·25	2·73
FeO ...	3·73	11·64	5·93	0·90
MnO ...	trace	—	—	—
MgO ...	19·66	14·68	15·12	22·40
CaO ...	0·11	—	0·68	0·20
SrO ...	trace	—	—	—
BaO ...	0·35	1·52	—	1·00
Na_2O ...	0·11	0·94	1·56	0·44
K_2O ...	10·59	8·66	9·35	10·70
Li_2O ...	nil	—	—	trace
H_2O- ...	0·19	—	0·45	—
H_2O+ ...	1·87	1·80	1·05	2·35
F ...	0·66	n.d.	n.d.	2·46
	100·15	101·36	100·08	100·74
$-O = F$	0·27			1·03
	99·88			99·71

I. Titaniferous phlogopite from phlogopite-leucite-lamproite Howe's Hill, West mberley area, Western Australia.

II. Biotite (meroxene) from shonkinite, Katzenbuckel, Odenwald, Germany. osenbusch, 1910, p. 201.)

III. Biotite from mica-peridotite, Kaltenthal, Harzburg, Germany. (Rosenbusch, 1910, p. 212.)

IV. Phlogopite from wyomingite, Leucite Hills, Wyoming. (Cross, 1897, p. 130.)

Other minerals.

Other minerals from the West Kimberley leucite-rocks include opside, leucite, and (?) nontronite. Of these the diopside is interesting it appears to be an almost pure diopside with γ 1·700. It is usually hedral and the forms developed are (110), (100), and occasionally 10). Most of the diopside shows lamellar twinning on (100). This neral has not yet been isolated for analysis.

The leucite is also very interesting as it shows alteration to a turbid aterial not unlike kaolin in appearance. Fresh leucite showing the aracteristic complicated twinning has been observed in one specimen

only. The analyses of these rocks indicate an excess of SiO_2 over that required to satisfy all the K_2O and Al_2O_3 in the form of orthoclase: the fine-grained base of these rocks must therefore be of very siliceous nature or the turbid alteration product of the leucite must contain much more SiO_2 than leucite. This material has certainly not had any K_2O removed from it by leaching. Further examination of this interesting mineral will be made when more material is available.

The remaining mineral of interest (? nontronite) occurs in the form of fibrous pseudomorphs after olivine. It is a bright green mineral with high birefringence and pleochroism after the scheme:

α yellow-green, $\beta = \gamma$ bright green. Absorption $\alpha < \beta = \gamma$.
α 1·595, γ 1·625, $\gamma - \alpha$ 0·030.

This mineral, therefore, appears to be a nontronite, and this is supported by the occurrence of cores of opal or quartz in the pseudomorphs.

Of the minerals described in the above pages, leucite, phlogopite, magnophorite, and an almost pure diopside, which are all abundant constituents of the West Kimberley lamproites, are present in the lamproites of the Leucite Hills, Wyoming, and Murcia, Spain. Occurrences of lamproites are rather rare and the common mineral associations in the three known lamproitic provinces mentioned above is interesting. The mineral magnophorite appears to be restricted to the lamproitic rocks, as no similar amphibole has been recorded from any igneous rocks other than the lamproites mentioned above. Phlogopite is also a rather rare mineral in igneous rocks, but the high potash and magnesia content of the lamproitic magma provides a favourable chemical environment for the separation of this mineral. No mineral similar to wadeite has been recorded from the Spanish or Wyoming areas, but the considerable zirconia content (0·22%) of the Wyoming rocks indicates the possibility of the occurrence of wadeite in these rocks.

Acknowledgements.—The research work on the igneous rocks of the West Kimberley area has been carried out at the Department of Mineralogy and Petrology, Cambridge, during the tenure of a Hackett Research Studentship from the University of Western Australia. The author desires to thank Dr. A. Wade, who collected the material, for permission to examine these rocks; Professor C. E. Tilley for his advice and criticism in connexion with this paper; and Mr. H. C. G. Vincent for making the analyses of the new amphibole and titaniferous phlogopite described above.

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An eyepiece micro-planimeter.

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[Read January 26, 1939; communicated by Dr. F. Coles Phillips.]

OCCASION arose recently when the writer required to make a number of comparative areal measurements of irregularly shaped portions of fossil corals in thin section, and it was found that the micrometric methods available were very tedious and involved considerable strain. A micro-planimeter has now been designed by means of which fairly accurate determinations of areas can be made with a minimum of eye strain. Though intended primarily for use with the petrographical microscope with the rotating stage, it can be adapted for use on microscopes of the fixed stage type.

The device takes the form of a photographically reproduced micrometer scale which fits into the eyepiece of the microscope in place of the ordinary micrometer scale used for linear measurements. The zero point of the scale is in the centre of the field of view at the intersection of two cross lines which are at right angles. The scale is graduated in such a way that the graduations marked 1, 2, 3 . . . 10 are at distances from the zero point proportional to the radii of concentric circles of areas 1, 2, 3 . . . 10 units (fig. 1). If, therefore, a circular object is placed on the stage of the microscope with its centre at the zero point of the scale, the scale reading of the position of the circumference would be a measure of the area of the object, and the true area could be found by multiplying the scale reading by a factor dependent on the magnification of the particular lens combination in use. If the object is not circular but of irregular outline, and a very large number of readings of the position of the edge of the object were taken at points at equal angular distances apart through a complete rotation of 360°, the object might be considered to be subdivided into a large number of segments of circles of different areas (fig. 3*a*). If n such readings are taken, then each reading gives the area of a circle n times the area of the segment for which that reading was taken. If, therefore, the total of the n readings is T, the average value T/n is proportional to the true area of the object, and the true area can be found by multiplying by an appropriate factor. If an infinite

ıber of readings is taken, the area so found must be the exact area, it is found in practice that a close approximation can be arrived at ı very few readings. For fairly regular objects twelve readings at ular intervals of 30° are usually sufficient, and with objects of ceme irregularity readings at 10° intervals give reliable results.

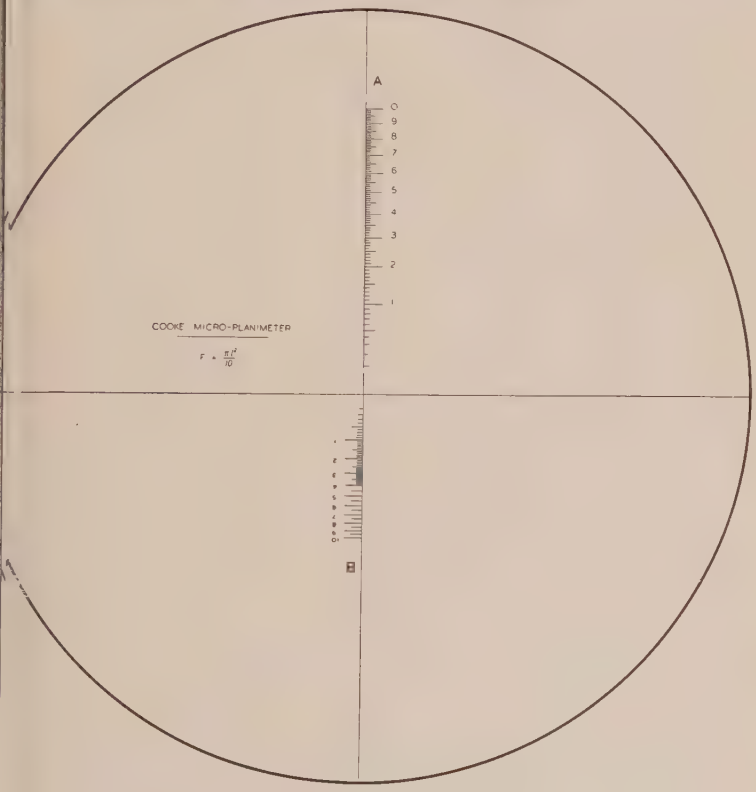

Fig. 1. The graduated scale comprising the micrometer.

he average of the readings taken is proportional to the area of the ect, but to determine the true area the average must be multiplied a factor depending on the lens combination in use. This factor can readily determined by measuring the apparent length of the plani- er scale, from the centre to the graduation marked 10, by means of age micrometer. If this length is l mm., then a circular object of ius l mm. would give, with the objective used, a reading of 10 units its area. Hence, since the true area is πl^2 sq. mm. and the apparent

area 10 units, the true area is found by multiplying the reading by a factor F such that $F = \pi l^2/10$, and this factor is a constant for the particular objective (used in combination with the eyepiece in question). Fig. 2 plots F in terms of l. True areas of any object measured with the particular objective will therefore be found by multiplying the average value T/n by the factor F for the objective. It is also at once apparent

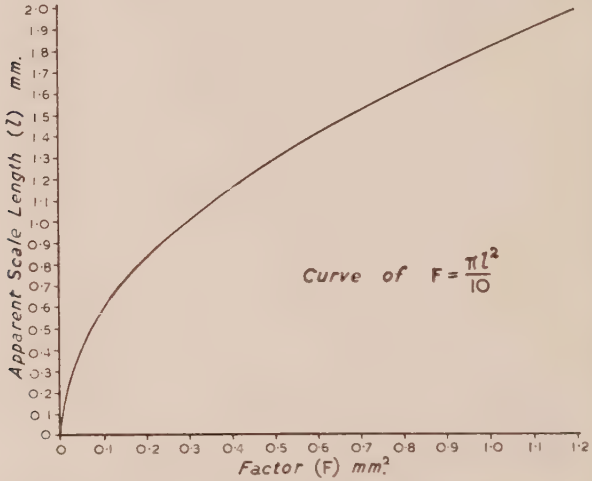

FIG. 2. Curve of the expression $F = \pi l^2/10$ for finding the value of the factor to be used in calculations with the micro-planimeter.

that a simpler factor ϕ can be used if n is kept constant. In this case the total of the readings T can be multiplied by ϕ, where $\phi = \pi l^2/10n$ or $\phi = F/n$, to give the same result, but it must be remembered that ϕ is dependent upon the value of n, and that F, and *not* ϕ, is the constant for the objective. From the formula, F may be determined for all the objectives in use, and this record should be kept with the microscope. It must, however, also be remembered that F takes into account the lower lens of the eyepiece in which the micrometer is mounted as well, and that a change of eyepiece may affect the factor. Since in practice only one eyepiece is generally fitted with a micrometer, this question does not commonly arise.

Two scales A and B have been incorporated in the micrometer, and are of exact known lengths, 5 mm. and 2·5 mm. respectively, though it has been found impossible for mechanical reasons to graduate B along the whole of its length. Two scales have been used because it was found

at the first division of the larger scale was not sufficiently finely aduated to enable small and large objects in the same section to be easured without changing the objective and thus altering the factor. nce the factor for B is one-quarter that for A, a ready conversion is ssible. Rotation of the eyepiece through 180° interchanges the posi-ons of the scales A and B, which are so arranged that confusion in ading is not likely to arise. When the micrometer is used in some eye-eces it will be found that the whole of scale A may not be visible. his in no way affects its utility, but since the whole scale is not visible r measurement of its length, scale B can be measured and the factor r A can be taken as four times that for B.

(Experimental designs were tested, using a number of scales at various gular inclinations to one another, with the object of reducing the mber of alterations which must be made in the angular position of e stage, but the simplest form seems best, since errors due to confusion e much less likely to occur.)

For use with microscopes with a fixed stage it is necessary to rotate e eyepiece relative to the object. A scale must be attached either to the croscope tube or to the eyepiece itself, and rotation effected against register mark on the component to which the scale is not attached. ch a scale must be made to fit the particular microscope upon which is to be used, and since the outer diameter of different makes of micro-pe tube differ so widely, it has not been possible to produce such a ale. It is a simple matter, however, to make one out of tin-foil, thick rdboard, or celluloid, and it need be graduated only every 10° with heavier mark every 30°. A spot of white paint on the edge of the eye-ece rim, or a second attached ring on the tube with a register mark on upper surface, enable quite accurate settings to be made. The attach-ent is used in the same manner as a cap analyser on petrographic icroscopes of the 'Dick' type. A deviation of one degree makes very tle difference to a reading, unless the edge of the object happens to be ry oblique to the scale.

In using the micro-planimeter it is essential that the microscope ould be accurately centred, since eccentricity on rotation produces ldditive or subtractive values on each reading with a total error quite sproportionate to the apparently small displacement at the centre. his disproportion will be seen to be accounted for by the fact that the gments into which the object is imagined to be divided are no longer contact along their edges, but either overlap or are separated by a rip of rectangular shape with one side the length of the displacement

of the centre from reading to reading. This is clearly shown in the diagram (fig. 3*b*) in which the eccentricity has been somewhat exaggerated.

Another precaution to be observed in taking readings is the avoidance of parallax errors due to the fact that the plane of the image does not always coincide with the plane in which the micrometer lies. If the eyepiece is fitted with a focusing eye-lens the focus can be adjusted to

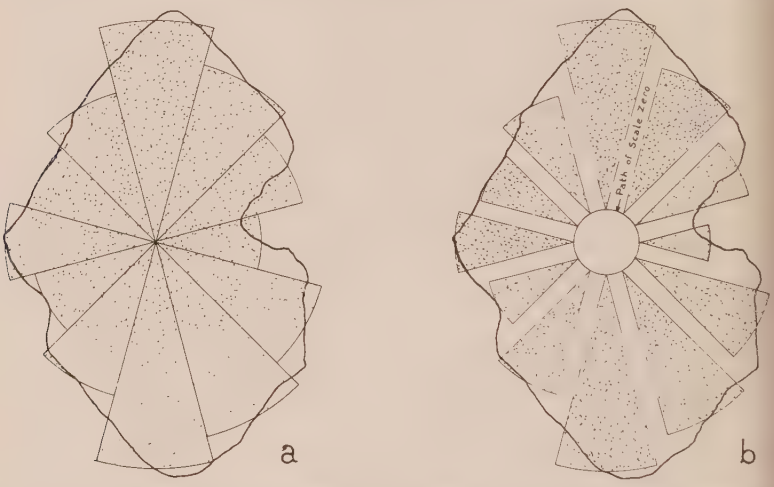

Fig. 3. Illustrating the error resulting from inaccurate centring of the objective. The stippled areas are the segments whose actual areas are measured. (*a*) is correctly centred and the actual error in the measured area is +0·34%. (*b*) is inaccurately centred and the error is obviously very large.

minimize this difference. It is advisable to use an objective of magnification such that the object to be measured fills about half of the field of view, and the centre of the object should be near the centre of the field. Before commencing readings, it is advisable to rotate the object completely to ensure that its outer edge does not at any point fall outside the limits of the scale.

Numerous experiments have been made to test the reliability of the micro-planimeter, both by measurements on regular objects of areas calculable from linear measurements (foraminifera, radiolaria, diatoms, well-formed crystals, and the like), and on irregular objects whose areas could be determined by other methods, such as the laborious one of 'counting squares' with a net ruling or of making determinations from camera lucida drawings both by ordinary planimetry or by the 'cutting out and weighing' method. As a result of the determinations it is

ssible to say that the error does not exceed $\pm 2\%$, provided that the mber of readings taken is suitably adjusted to the degree of irregu- ity of the object.

It has been used with advantage wherever comparative areal or volu- tric measurements are needed. Notable amongst these uses in minera- gy is its application to solving the problem of the composition of ned felspars, since it is possible to use the instrument under crossed cols if the stage is kept fixed and the eyepiece moved, or the nicols are ated periodically so that the boundaries of the different zones are ways distinct. It has also been used to find the relationship between luded crystals and their hosts; to find the degree to which decomposi- n has advanced in crystals; to determine volumetrically the changes ing place in hydrothermal alteration of minerals; and other similar es. In petrography it has been used both for making comparative asurements regarding coarseness of crystallization in different phases an igneous intrusion and in obtaining modal analyses. In this latter e analyses accurate enough for the determination of the rock under hannsen's[1] scheme of classification can be very quickly made, since h mineral grain can be measured in two to three minutes or even less. e method adopted has been to draw a rectangle of known area on the er-glass of the section by means of a stencil and then to determine area of each constituent mineral within the rectangle, or a mask a rectangular aperture may be stuck directly on the cover-glass. e accuracy of the method has been proved by performing comparative ts with the Shand or Dollar integrator and the micro-planimeter, and e economy of the latter may enable it to be used where the expensive d heavy instrument is not available.

It may be noted that where comparative areas only are required, and ly one objective is being used, it is necessary only to compare the ues of T, provided n is also kept constant. If n is not the same for all observations, T/n values can be compared, still without the necessity taking F into account. If different objectives are used, however, the e areas only must be used.

The micrometer is now obtainable to order from Messrs. E. Leitz of etzlar, Germany, or through their agents, and will be known as the *Cooke cro-planimeter*. It has been made primarily to fit the eyepiece specially anufactured by that firm for the reception of micrometers of all types, t it will be possible to fit it in any make of eyepiece where the micro-

[1] A. Johannsen, A descriptive petrography of the igneous rocks. 1931, vol. 1, . 140–158.

meters are interchangeable. It has also been made of such a size that it can conveniently be used in eyepieces giving a wide field of view, and when it is to be used in microscopes having the narrow tube, it is strongly recommended that the Leitz periplanatic eyepiece for the reception of micrometers be used, as this eyepiece alone out of a large number which were tried enables the whole of both scales to be visible in the field. In eyepieces having a diaphragm less than one centimetre in diameter, the whole of scale A will not be visible, though this does not impair the utility of the device.

The writer wishes to express his indebtedness to Mr. D. R. Robinson for his helpful advice and co-operation in solving problems of design, and particularly for his kindness and skill in drafting the originals from which the experimental and final micrometers were reproduced. He wishes also to thank Dr. F. Coles Phillips for his interest and assistance in preparing and presenting this paper.

The composition of francolite.

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[Read January 26, 1939.]

Introduction.

N 1850, T. H. Henry[1] published an imperfect analysis of francolite, a supposed new mineral, previously named by H. J. Brooke. Henry ted that his material was similar to the material from Wheal Franco, vistock, Devon, but he does not show how he was in a position to ow the composition of the material from this mine, because there is record to indicate that the mineral from Wheal Franco had been lysed. Henry did not report CO_2 for the material he analysed, but H. N. Story-Maskelyne and W. Flight[2] analysed material, supposedly ilar, and obtained a significant amount of CO_2. Their determinations as follows:

CaO.	P_2O_5.	CO_2.	F.	H_2O.	Na_2O.	$FeO+MnO+Fe_2O_3$.
44·09	38·14	2·25	3·34	1·59	0·69	0·91

ese authors state that the mineral from Wheal Franco contains CO_2 o, but they do not give any determinations for material from this ne. Their material is now known to have come from the Fowey nsols mine, St. Blazey, Cornwall.[3] H. Robinson[4] analysed, under the ne francolite, material from the Levant mine, St. Just, Cornwall.

Although Brooke apparently proposed the name francolite and nough he seemingly did not publish any description of the mineral,

[1] T. H. Henry, Phil. Mag., 1850, ser. 3, vol. 36, p. 134.
[2] M. H. N. Story-Maskelyne and W. Flight, Journ. Chem. Soc. London, 1871, 24, p. 3.
[3] R. H. Solly, Min. Mag., 1886, vol. 7, p. 57.
[4] H. Robinson, Min. Mag., 1886, vol. 7, p. 59.

Henry's description is not the earliest appearance of the name. A printed sale catalogue, issued by the mineral dealer H. Heuland, lists francolite among the minerals offered for sale on May 15, 1843.

Thus it seems that, although three analyses have been recorded for francolite, none of the specimens came from Wheal Franco, and there remained some doubt as to the composition of the mineral named by Brooke.

In 1866, C. A. Stein[1] described the phosphorite from Staffel, Nassau, introducing the name staffelite for a calcium phosphate containing carbon dioxide, and this was done prior to the appearance of a reliable analysis of francolite. From the data for francolite given by Story-Maskelyne and Flight and for staffelite given by Stein, A. Lacroix[2] has supposed francolite and staffelite to be identical. This view is confirmed by a new analysis of staffelite recently given by J. W. Gruner and D. McConnell[3] and by the new analysis of francolite to be presented below.

The specimen now investigated is B.M.61342 of the British Museum collection, which was found unlabelled and was registered in 1883, but which is almost certainly identical with B.M.15628, a specimen obtained at Heuland's sale in 1843 and the specimen referred to in his sale catalogue (lot 154). It is therefore almost certainly from Wheal Franco, and the actual specimen to which the earliest public ascription of the name francolite was made.

Physical and Optical Properties.

The specimen consists of clear, colourless francolite, forming a thin, confusedly crystalline crust on a fibrous quartz mass which is heavily impregnated with haematite.

The density was determined by flotation in Clerici solution as $D_4^{21} = 3{\cdot}178 \pm 0{\cdot}006$, and by the micro-pyknometer[4] as $3{\cdot}173 \pm 0{\cdot}020$ (calculated probable error for a single determination). The material was separated from haematite and quartz through the use of bromoform and Clerici solution and with an electromagnet. A microscopic examination showed the material to be free from impurities except for small amounts of haematite and quartz, which could not readily be removed without considerably reducing the small samples available. Failure to remove

[1] C. A. Stein, Jahrb. Ver. Naturk. Nassau. 1866, vol. 19 20, p. 41; Neues Jahrb Min., 1866, p. 716.

[2] A. Lacroix, Compt. Rend. Acad. Sci. Paris, 1910, vol. 150, p. 1213.

[3] J. W. Gruner and D. McConnell, Zeits. Krist., 1937, vol. 97, p. 208. [M.A 7–88.]

[4] F. A. Bannister and M. H. Hey, Min. Mag., 1938, vol. 25, p. 30.

uartz completely is of little significance. The failure to remove haema-ite completely probably accounts for most, if not all, of the soluble iron btained on analysis. These impurities together represent the insoluble natter shown in the analysis. No trace of calcite or other carbonate ould be seen, and all grains alike can be seen to give off bubbles of carbon ioxide during solution in acid. There is certainly no admixture of free alcite or other carbonate, as suggested by J. Thewlis, G. E. Glock, and M. M. Murray,[1] in this material.

The material is not well suited to optical examination as individual rystals cannot be isolated. Most of the grains show sharp extinction nd no appreciable departure from uniaxiality. A few show division nto sectors extinguishing at about 60° to one another with very weak irefringence and a small optic axial angle; none of these grains showed rystal faces, and the boundary between adjacent sectors is mostly rregular and useless for a reference line, hence no measurements on the ptic orientation could be made. A few basal grains showed division nto sectors, each sector being subdivided into fine lamellae of irregular idth, arranged parallel to the edges of the basal plane, the lamellae aving alternately weak and very weak birefringence, straight extinc-on, and positive elongation. The refractive indices were determined y the immersion method, which gave ω 1·629, ϵ 1·624, both $\pm$0·002.

Chemical Data.

The specimen available was sufficient only for semi-micro methods of nalysis. The most abundant constituents were determined by the semi-nicro methods on an analysed specimen of staffelite before attempting hem on the small sample of francolite from Devon. The staffelite had een analysed by Dr. R. B. Ellestad (in Gruner and McConnell, 1937, c. cit.), and the results obtained by the semi-micro methods compare with his results as follows:

	CaO.	P_2O_5.	CO_2.	H_2O+.	H_2O-.
Macro (Ellestad)	54·88	37·71	3·36	1·14	0·04
Micro (E. B. S.)	54·78	38·05	3·24	1·25	0·03

These determinations are sufficiently similar to indicate that the semi-nicro methods used for this work are quite comparable to the methods which required larger samples. The results agree within 0·1%, except for P_2O_5, where the semi-micro method yielded a result about 0·3% nigher than the macro method.

[1] J. Thewlis, G. E. Glock, and M. M. Murray, Trans. Faraday Soc., 1939, vol. 35, p. 358. [M.A. 7–352.]

Calcium, magnesium, and phosphorus were determined essentially by the method given by Hoffman and Lundell[1] for the analysis of phosphate-rock. Calcium was separated by double precipitation as the oxalate at a *pH* of 3 to 4 and weighed as the carbonate by igniting the precipitate at 475–525° C. In the determination of magnesium, calcium was first separated as sulphate in alcoholic solution, and magnesium was then precipitated in the filtrate as magnesium ammonium phosphate in the presence of citrate after removal of the alcohol; the magnesium ammonium phosphate was weighed as the hexahydrate after washing with acetone and air-drying. Phosphorus was separated from the other constituents of the sample by two precipitations with magnesia mixture in the presence of ammonium citrate, without preliminary precipitation with molybdate, and weighed as magnesium pyrophosphate.

Carbon dioxide was determined gravimetrically by absorption in 'ascarite' (soda-asbestos) after liberation with dilute hydrochloric acid. Total water was determined by the Penfield method, lead oxide being used as a retainer for fluorine. Insoluble material was determined by treating the sample with dilute hydrochloric acid and drying the residue at 105° C. Iron in the hydrochloric acid solution of the sample was obtained by precipitating as sulphide in ammoniacal solution containing tartrate, dissolving the precipitate in hydrochloric acid, oxidizing with bromine water, and finally applying the colorimetric thiocyanate method.

Twenty milligram samples were used in the determination of calcium, phosphorus, and total water, and a 40 mg. sample for carbon dioxide. The filter-stick technique was applied in the determinations involving precipitation, and when the precipitate was to be ignited at a high temperature a porcelain filter-stick was employed in conjunction with a 10 ml. platinum crucible as the precipitation vessel.

Dr. W. D. Armstrong kindly determined the fluorine on several samples weighing between 5 and 10 mg. through the use of his modification[2] of the method of H. H. Willard and O. B. Winter.[3] The end-points were quite distinct because interfering substances were apparently absent. The value reported is an average of three determinations: 3·69, 3·68, and 3·77.

The results of the analysis are given in table I, and are discussed below. A spectroscopic analysis of the specimen was obtained and it indicated the presence of Mg, Cu, Be, Fe, Mn, Sr, Pb, Si, Bi, and Zn, but none of these were determined chemically except Mg and Fe, and there is no reason to believe from the intensities of the lines on the spectrogram that any of these elements are present in greater abundance than 0·1% (except Fe) and most of them are probably less abundant than 0·01%.

X-Ray Data and Interpretation.

The specimen was examined by the powder diffraction method[4] and the lattice constants were obtained as a 9·34, c 6·89 Å. (both $\pm$ 0·01),

[1] J. I. Hoffman and G. E. F. Lundell, Journ. Res. Nat. Bur. Standards, U.S.A., 1938, vol. 20, p. 607.

[2] W. D. Armstrong, Journ. Amer. Chem. Soc., 1933, vol. 55, p. 1741.

[3] H. H. Willard and O. B. Winter, Ind. Eng. Chem. (Anal.) 1933, vol. 5, p. 7.

[4] We are indebted to Mr. Lynn Gardiner, of the University of Minnesota, for the preparation of the powder diffraction photograph.

$\alpha = 0{\cdot}738$. The interplanar distances obtained with Fe-K_α radiation a camera of 57·3 mm. radius are given in table II, where they are mpared with an analysed sample of fluor-apatite from Hastings D., Ontario.[1]

ABLE I. Chemical analysis (by E. B. Sandell) of francolite (B.M.61342) from Wheal Franco, Buckland Monachorum, Tavistock, Devon.

	Weight per cent.		Unit-cell contents* i.	ii.
CaO ...	53·94	Ca ...	9·83	9·73
MgO ...	0·10	Mg ...	0·02	0·02
P_2O_5 ...	38·13	P ...	5·49	5·43
CO_2 ...	3·40	C ...	0·79	0·78
F ...	3·71	F ...	1·99	1·97
H_2O+ ...	0·46	OH ...	0·52	0·52
H_2O- ...	0·01	O ...	23·90	23·70
Fe_2O_3 ...	0·34	Total ...	42·54†	42·16†
Insol. ...	1·83	O+OH+F	26·41	26·19
	101·92	C in Ca positions	0·28	0·21
Less O ...	1·56			
Total ...	100·36‡			

* Calculated from the cell sides, density, and analysis; (i) assuming a density of 178, (ii) a density of 3·145.

† $\pm 0{\cdot}30$. ‡ SO_3, Cl, absent.

From these cell sides, the density, and the chemical analysis, the mber of atoms of each kind in the unit cell may be computed, and the sults of these calculations are included in table I. Unfortunately, the esence of haematite films on the crystal fragments makes it almost rtain that the observed density of 3·178 is distinctly too high. If the hole of the 1·83% insolubles found could be taken as haematite, the rrected density would be $3{\cdot}145 \pm 0{\cdot}006$, and calculations were there- re made based on both these densities; the true figures must be some- here between these extremes.

If, instead of calculating the cell contents from the density and other xperimental data, the density is calculated from the cell sides and nemical analysis on the assumption that the unit cell contains 42 atoms ltogether, a value of $3{\cdot}139 \pm 0{\cdot}015$ is obtained; calculating on a basis of 6(O+OH+F) in the unit cell, the density should be $3{\cdot}129 \pm 0{\cdot}015$.

From these calculations, which show reasonably good agreement, two

[1] A. S. Dadson, Univ. Toronto Studies, Geol. Ser., 1933, no. 35, p. 51. [M.A. 5–480.]

conclusions may be drawn. First, it is probable that the 0·46% of H_2O+ shown in the analysis is not wholly water of constitution; if it is assumed that the unit cell contains 42 atoms altogether and 26

TABLE II. Powder diffraction diagram of francolite.

Unfiltered Fe radiation; $R = 57{\cdot}3$ mm.

		Fluor-apatite.		Francolite.	
No.	Indices.	*d*.	*I*.	*d*.	*I*.
1.	(002)	3·432	2	3·428	3
2.	(102)	—	—	3·157	½
3.	(120)	3·060	3	3·058	3
4.	(300)β	2·975	½	2·965	½
5.	(202)β	2·884	½	—	—
6.	(121)	2·798	10	2·795	10
7.	(112)	2·769	4	2·765	3
8.	(300)	2·702	6	2·694	6
9.	(202)	2·616	3	2·618	3
10.	(301)	2·517	½	—	—
11.	(130)β	2·477	½	—	—
12.	(122)	2·289	½	2·286	½
13.	(130)	2·248	2	2·244	2
14.	(131)	2·135	1	2·130	1
15.	(113)	2·057	1	*	—
16.	(123)β	2·026	½	2·024	1
17.	(203)	2·001	½	*	—
18.	(222)	1·937	3	1·934	4
19.	(132)	1·883	1	1·883	1
20.	(123)	1·838	6	1·837	6
21.	(231)	1·795	3	1·795	2
22.	(140)	1·769	3	1·768	2
23.	(402)	1·745	3	1·746	2
24.	(004)	1·720	3	1·722	3
25.	(232)	1·637	1	1·635	1
26.	(133)	1·605	½	—	—
27.	(240)	1·533	½	—	—
28.	(331)	1·521	½	—	—
29.	(124)	1·498	1	1·502	½
30.	(502)	1·468	2	1·470	1
31.	(304)	1·452	1	1·456	1

* Indistinct lines occurred in these positions.

(O+OH+F), and that the remainder of the analysis is accurate, the essential water should be only 0·11%, and the calculated density 3·141 ±0·015. Secondly, it is clear that there is a definite substitution of calcium by carbon, to the extent of approximately 0·2 atoms per unit cell,[1] the remainder of the calcium (about 0·6 atom per unit cell) replac-

[1] Calculations of atomic ratios have also been made to bases of (O+OH+F) = 26, of (Ca+Mg+P+C) = 16, and of total atoms = 42; all agree in showing approximately 0·2 atom carbon replacing calcium.

g phosphorus. This type of substitution has been demonstrated also r francolite (staffelite),[1] ellestadite,[2] and dahllite,[3] while a recent alysis by H. C. G. Vincent[4] (T. Deans, 1938) of francolite from Robin ood quarry, Thorpe-on-the-Hill, Leeds, indicates carbon replacing osphorus, but not calcium. In the present case, definite evidence was tained that the material was quite free from calcite or other carbonates. N. V. Belov[5] suggests that it is structurally improbable that carbon ould replace calcium atom for atom, but quite possible that one carbon ay replace two of those calcium atoms which lie on the three-fold axes, d such an interpretation is quite consistent with the present analysis. t while the data clearly demonstrate that carbon does replace lcium, they are not sufficient to decide whether the replacement is $\rightleftharpoons$Ca or C$\rightleftharpoons$2Ca.

Conclusions.

Francolite and staffelite are identical, and the name francolite has riority. A specimen obtained from the British Museum has been alysed by semi-micro methods and a general description of the method given. The lattice constants and physical and optical properties have en measured and found to be mutually consistent within the limita- ns of the methods. Carbon was found to enter the apatite lattice in e calcium and phosphorus positions (as previously postulated for veral other carbonate-apatites) on the basis of the analysis, to form CO_3-groups similar to those found in calcite and aragonite in the first stance, and CO_4-groups with a tetrahedral configuration in the second stance. This is the fourth analysis of a carbonate-apatite to confirm ese conclusions.

[1] J. W. Gruner and D. McConnell, 1937, loc. cit.
[2] D. McConnell, Amer. Min., 1937, vol. 22, p. 977. [M.A. 7–14.]
[3] D. McConnell, Amer. Journ. Sci., 1938, ser. 5, vol. 36, p. 298. [M.A. 7–351.]
[4] T. Deans, Min. Mag., 1938, vol. 25, p. 135.
[5] N. V. Belov, Compt. Rend. (Doklady) Acad. Sci. URSS, 1939, vol. 22, p. 89. [M.A. 7–351.]

On the presentation of chemical analyses of minerals.

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[Read March 9, 1939.]

THE results of a chemical analysis of a mineral are always presented, in the first place, as percentages of elements or oxides present,[1] and until recently the only possible further treatment of these values was to calculate atomic or molecular ratios, group them according to accepted isomorphous groups, and deduce (if possible) an integral chemical formula. The degree of approximation to integral ratios accepted as satisfactory is, of course, quite arbitrary, and a decision as to the degree of complication acceptable in a chemical formula has often had to rest on very inadequate evidence. Some workers prefer to adjust the final ratios to show the errors evenly distributed, a procedure which has no real advantages.

The introduction of X-ray methods of structure analysis, and the measurement of the actual sizes of the structural units of many minerals, has opened the way to much more significant methods for the presentation of chemical analyses, and there is now rarely any justification for guesswork in the assigning of a chemical formula. Unfortunately, the possibilities and the limitations of a presentation based on structural data are not always realized and it is the purpose of this note to call attention to some points in this connexion.

Wherever an accurate determination of the density and unit-cell size of the mineral has been made on the actual material analysed, the most satisfactory presentation of a chemical analysis is in atoms, ions, or molecules per unit cell of the several constituents shown by the analysis;

[1] Often, most of the oxides shown in an analysis were actually weighed as such. This has one advantage not often realized; it is not necessary to know the atomic weights used by the analyst in order to make use of the analysis. This may seem unimportant, but is not always so; thus in any analysis of an antimony mineral, Sb will probably be reported as the element after weighing as Sb_2S_3, and the percentage Sb reported will be appreciably different according as 120·2 or 121·76 is used as the atomic weight of Sb. A note on the weighing-forms and atomic weights employed is certainly desirable in any analysis having claims to high accuracy.

these may be styled empirical unit-cell contents as distinct from those 'unit-cell contents' referred to below, which are really atomic ratios to a more or less arbitrary basis. Such a presentation involves no assumptions whatever, and carries the greatest possible conviction, especially when a new chemical formula is being proposed. It has one disadvantage, that the accumulated errors of the density and X-ray measurements are applied to the chemical data, but this cannot be regarded as serious. There are, however, certain limitations to its use, and certain precautions necessary if it is to be used to full advantage, not always recognized.

If the analysis shows any impurities, their nature should be ascertained and the density corrected accordingly,[1] if possible; if the density cannot be accurately corrected for the impurities, it will at least be possible in almost every case to assign limits to the probable true density. It is not necessary to recalculate the analysis to 100%, whether impurities are present or not; a more convenient procedure is to compute the atomic or molecular ratios, P/M, for each constituent[2] by division of its percentage, P, in the mineral by its molecular weight, M, and then find a conversion factor F by which to multiply the atomic ratios to give cell contents FP/M directly; if the cell volume is V and the density (corrected for any impurities) D, then $F = VD/1{\cdot}649S$, where S is the net summation of the analysis after subtraction of impurities.[3] Further, the probable percentage error in F should be calculated from the known or assessed probable errors in the cell sides and density. This is relatively simple and can nearly always be effected, but probable errors in the chemical analysis are much more difficult to assess; the accuracy attainable in chemical analyses has been discussed by W. F. Hillebrand and G. E. F. Lundell[4] and by E. S. Larsen,[5] and it is evident that where any

[1] Where the impurity is adsorbed water, it is not really certain what density should be assumed for the water; however, a value of 1 is not likely to introduce appreciable error.

[2] Most mineral analyses are primarily presented in a mixed form, mainly as oxides, but with some negative ions (F′, Cl′, S″), and 'less O for' these latter. To deduce the atomic ratio for oxygen a formal calculation of the percentage of oxygen is unnecessary; the molecular ratios of the several oxides are multiplied by the number of oxygen atoms in each oxide added, and the atomic ratio for any oxygen subtracted 'for F′, Cl′, &c.' subtracted from the sum.

[3] These relations may seem too obvious to require stating, but instances could be cited from the recent literature where corrections for impurities have been wholly neglected and conversations have shown that the way in which a correction may be effected is often not understood.

[4] W. F. Hillebrand and G. E. F. Lundell, Applied inorganic analysis. New York, 1929.

[5] E. S. Larsen, Amer. Journ. Sci., 1938, ser. 5, vol. 35, p. 94. [M.A. 7–183.]

unusual type of isomorphous substitution is postulated the magnitude and effect of possible errors in the analysis should receive especial consideration.

As a general rule, the calculation of empirical unit-cell contents shows that the several kinds of atoms present, when divided into groups on well-established lines, add up to integral numbers (within the limits of the probable errors of the chemical analyses, and of the cell-side and density determinations[1]) and can be assigned to the several lattice positions of the crystal-structure; but it must not be assumed that this will necessarily be the case, and that a failure to attain integral relations indicates an inaccurate analysis. Recent work has shown that vacant lattice positions are comparatively frequent, and the possibility of an excess must not be disregarded, though in general an excess probably indicates an error.

By far the most troublesome constituent of minerals for the satisfactory presentation of a chemical analysis is water, since it may be present adsorbed, when it constitutes an impurity, or as hydroxyl groups, or as molecular water of crystallization, and the accurate distinction of the three forms is rarely possible. As a general rule, small quantities of water lost at a low temperature may be assumed to be adsorbed, but the distribution of water into impurity and constitutional (including water of crystallization) is often essentially arbitrary and constitutes the most serious weakness in the determination of empirical cell contents.

The effect of adsorbed water, not recognized as an impurity, on the calculated cell contents deserves special consideration since it is one of the most difficult of all impurities to detect, even when present to the extent of several per cent. The observed density will be low, but the oxygen atoms per unit cell (including the oxygen of the water) will usually be high,[2] and the other atomic contents low. Now in a large proportion of minerals the oxygen atoms (or more generally, O'', OH', and F' ions) are the largest atoms present and there is no room for an

[1] It must, of course, be remembered that these last, affecting the factor F, will necessarily affect all constituents equally or in the same direction, and cannot affect their distribution.

[2] The low density makes the factor F low, but because water contains a larger percentage of oxygen than any other compound the oxygen percentage will be high, and as a general rule the latter effect will preponderate; as an illustration we may calculate the effect of 1 per cent. adsorbed water on the apparent cell contents of quartz and of litharge: Si 2·951, O 6·002, H 0·199 (in place of Si 3, O 6); Pb 1·962, O 2·208, H 0·491 (in place of Pb 2, O 2); the effect is, of course, more marked the smaller the percentage of oxygen in the substance.

cess of them; hence if the oxygen atoms per unit cell appear to exceed e most probable integral value by more than the probable error of the ctor F, adsorbed water may usually be suspected—to prove it is nother matter.

In minerals containing much constitutional water (hydroxyl or water crystallization), and especially in deliquescent or efflorescent salts, e uncertainty of the water content makes the calculation of reliable nit-cell contents difficult or impossible; the same difficulty may arise ith certain iron minerals which are not readily opened up (such as aurolite), when the uncertainty as to the division of the total iron into rrous and ferric renders the total oxygen content uncertain. In such ses it may be preferable to have recourse to one of the several presen- tions based on an assumption. Such forms of calculation are also luable for presentation of numbers of analyses from the literature (for w of which correlated density and X-ray data are likely to be avail- le), or when for any reason adequate accuracy in the X-ray or density ta is not attainable.

The first essentials in all presentations based on an assumption are that e basic assumption should be clearly and explicitly recognized, should carefully selected to suit the particular circumstances, and that there ould be adequate evidence in justification of it. Such evidence of stification will normally take the form of analyses with correlated nsity and X-ray data, from which empirical unit-cell contents sup- rting the proposed assumption are calculated. Or it may be shown at the compound in question is isomorphous with another for which e validity of the proposed assumption has been demonstrated, and that ere is reason to believe the extension justified. Or the assumption may e that X-ray (or more rarely, density) measurements made on a sample ier than the actual sample analysed[1] are accurate enough for use in the lculation of the analysis, when evidence is desirable that the cell-sides r density) of the species in question do not vary appreciably, or that ey vary in regular manner, so that the values for the sample analysed ay be fairly deduced from its composition.

When X-ray or density data, or both, are lacking or inaccurate it is longer possible to calculate the empirical cell contents. But since the mber of lattice positions available for any atom or group of atoms in crystal-structure is always integral, and since in many cases all, and in

[1] It is most unscientific for chemical analysis and optical, X-ray, or other physical ta to be made on separate samples without explicit statement of the fact, and a reful check of the uniformity of the material studied is always desirable.

almost every instance some group or groups of lattice positions are exactly occupied,[1] without excess or defect (within the accuracy of experiment), it is often justifiable to assume that the unit-cell contents of the specimen analysed will show an integral value for some atom or group of atoms,[2] and to calculate atomic, molecular, or ionic ratios on this basis; such ratios are often wrongly called unit-cell contents, but they are really no more than atomic ratios to an arbitrary basis, and should always be so described, specifying the basis assumed.

The most suitable basis to use for presentation will vary, not only with the type of mineral under examination, but also with the purpose of the presentation; thus to provide convincing evidence of an unusual isomorphous substitution, that basis of calculation should be selected which reduces the substitution to be proved to a minimum, so that any other basis of calculation gives a greater apparent degree of substitution.[3] The principal types of minerals for the present purpose are: (i) those whose analyses which are usually reported mainly or wholly in terms of oxides, whose largest ions are O'', OH', and F', and in which it is not possible to select groups of constituents, failure of which to balance necessarily indicates an inaccurate analysis; (ii) minerals whose analyses are usually reported in terms of ions, which must necessarily balance in an accurate analysis—for example, halides;[4] (iii) 'atomic' minerals whose analyses are reported in terms of atoms, such as sulphides and selenides, but which differ from the formally similar ionic minerals in that there is often no exact balance (as in the well-known case of pyrrhotine). There are some broad distinctions as to the most suitable basis of calculation for each of these types, though each individual case must be considered on its own merits.

Among minerals normally reported in terms of ions the fact that

[1] The electrical conductivity of some ionic crystals which show no excess of either component is probably due to vacant positions in both anion and cation lattices; proof of this suggestion appears to be still incomplete, and the proportion of vacancies called for is very small (up to 0·02 per cent. in calcite).

[2] The actual integer to be accepted may be decided on the basis of approximate unit-cell contents, based on an approximate density and cell-sides, or by extension from an isomorphous or isostructural compound.

[3] Thus in evidence of the substitution of C for Ca in carbonate-apatites, it was shown that no basis of calculation of the analyses could be found requiring less of this substitution than 0·2 atom per unit cell. (This vol., p. 400.)

[4] Recent work has shown that even so typically ionic a mineral as rock-salt may contain an excess of sodium ions, balanced only by free electrons; such excess is usually far less than the probable accuracy of the majority of analyses, but clearly an ionic balance need not always be quite exact.

positive and negative ions must balance may be used to classify analyses s to their probable accuracy, and the most suitable basis of calculation ill normally be to give an integral value to the sum of all the ionic harges[1] (Σ(ionic charge) = const.), but occasionally other bases may e preferable. The same method may be used in salts which are normally pported in terms of oxides, such as sulphates, if there is definite evidence hat the salt has an ionic structure and is not contaminated with any cidic or basic impurity. With hydrated salts, it will generally be prefer- ble to exclude the water from the sum to which an integral value is ssigned, since it is the component most likely to be affected by analy- cal error; departure of the water content from an integral ratio may hen indicate either impurity, an inaccurate analysis, or that the hydrate of the zeolitic type.

In minerals such as sulphides and selenides, where vacant lattice ositions are very common, it is generally best to assume that one group f atoms (metal or sulphur, &c.) occupy an integral number of lattice ositions and the other group have vacant positions; but the possibility f extra interstitial atoms, or of the replacement of sulphur atoms by sul- hur pairs in some structures,[2] must not be ruled out without direct proof. mong these minerals it is generally impossible to discuss the probable ccuracy of an analysis on internal evidence, which is especially unfor- nate, as many analyses of sulphide minerals are of doubtful accuracy.

Among silicates and other minerals which are normally reported in rms of oxides, the majority of structures show great possibilities of omorphous substitution, but in most cases it is justifiable to assume hat the sum of the large ions, $O'' + OH' + F'$, will be integral and to use his as a basis of calculation ($\Sigma(O'' + OH' + F') = \text{const.}$). For anhydrous inerals this usually is a simple matter,[3] and where the water can be

[1] The possibility that an ion may be replaced by one of a different charge without he creation of a lattice vacancy must not, however, be forgotten; neutrality could maintained by interstitially accommodated ions or by a simultaneous parallel bstitution among the ions of opposite sign.

[2] Another possibility is that sulphur atoms may enter some of the metal positions, vice versa. In any particular sulphide or similar mineral, calculations to an ssumed basis can do no more than demonstrate variability and departure from a nstant simple metal sulphur ratio; the manner of this variation can only be rofitably discussed on a basis of empirical cell contents, at least in the present ate of our knowledge of such structures.

[3] The exception is with minerals where the determination of the state of oxidation such elements as Fe, Mn, or V is liable to be inaccurate from the nature of the ineral (e.g. staurolite). For such minerals Σ(cations) = const. will often be a more tisfactory mode of presentation.

shown to be wholly water of crystallization, as in zeolites, it is best to exclude it from the oxygen sum, but hydrous silicates including both hydroxyl and water of crystallization give rise to more serious problems owing to the possibility that the water positions may be incompletely filled or that there may be appreciable amounts of adsorbed water. In some cases it may be possible to find another satisfactory basis of calculation, but in others, such as the clays, there does not appear to be any really satisfactory basis available. Calculations to an 'anhydrous basis' amount to an additional assumption that the number of hydroxyl groups per unit cell is constant; this is certainly not the case in the micas, and there is no apparent reason why it should be even approximately true in the clays. In general, if $(O'' + OH')$ cannot be accurately determined and there is no evidence that OH' is likely to remain constant, a really satisfactory basis of presentation of the chemical analysis will rarely be found.

It is possible that a distinction between hydroxyl and water of crystallization or adsorbed water might be obtained by the use of deuterium oxide, since the ease of hydrogen exchange is likely to vary widely with the binding; no experiments appear to have been made as yet in this direction, but we would suggest that it may be found a useful tool in work on hydrous minerals.

When calculations of analyses are made to an assumed integral number of atoms per unit cell of some constituent or group of constituents, $\Sigma R = K$, on material for which X-ray data are available, it is usual to calculate the density on the basis of the analysis, X-ray data, and assumed integral number K; using the same symbols as above, it is clear that if $\Sigma(P/M)$ indicates the sum of the atomic ratios P/M for the several constituents included in the sum K, the conversion factor $F = K/\Sigma(P/M)$, and hence $D(\text{calc.}) = 1{\cdot}649SF/V = 1{\cdot}649SK/V\Sigma(P/M)$. The probable percentage error in D(calc.) will be equal to that in V, plus an unknown amount due to errors in the chemical analysis or to departures from the assumed integral value $\Sigma R = K$ atoms per unit cell. This value D(calc.) is of course a calculated density of the pure mineral, and is to be compared with the observed density as corrected for impurities.

In a form of presentation which is occasionally seen, the atomic ratios, except that of oxygen, are first calculated on an assumed value for the total cations per unit cell, and the oxygen ratio is then taken by difference from an assumed value for total anions per unit cell $(O'' + OH' + F'$, usually); anionic and cationic charges or valencies are then totalled and

ompared, and any failure of them to balance[1] is taken to indicate naccuracy of the chemical analysis or undetected impurities in the naterial. This mode of presentation has much the same value and applinability as an ordinary calculation to an assumed total number of cations er unit cell. It has the disadvantage that the results are liable to be misunderstood by those not familiar with the method and that it throws ne whole of the experimental errors on one constituent, oxygen.

Whatever form of presentation is used, the figures shown will be ffected by any inaccuracies in the chemical analyses, which may take nree forms: either (i) a constituent may have been accurately separated, ut inaccurately determined, when that constituent (and the sum) will e low or high, the other constituents being correct, or a separation may e imperfect, when one constituent will be low and another high by i) the same or (iii) a different amount;[2] and (iii) may be formally treated s a combination of (i) and (ii).

In an analysis reported in terms of oxides and presented as empirical nit-cell contents, an error of separation whereby some of an oxide $_mO_n$ (of molecular weight a) is reported as B_pO_q (of molecular weight b), he calculated oxygen atoms per unit cell will be high if $am/n < bp/q$, but eyond this, only the elements A and B actually involved in the separaion will be affected. An error of determination, on the other hand, will ffect all constituents; if $x\%$ of the oxide A_mO_n is lost, all the other onstituents will be high by a factor $(1+x/100)$; oxygen may be low or igh.[3]

When the analysis is presented as atomic ratios to an assumed basis, nalytical errors may have very different effects according to the basis f calculation adopted. Thus if the adopted basis is Σ(cations) − const., n error of separation will affect the calculated density and the ratios or all the constituents equally except oxygen and the two constituents irectly involved, the effect being an increase if $a/m < b/p$ (symbols and

[1] Except in this form of calculation, anionic and cationic charges or valencies nust necessarily balance in analyses which are presented mainly in the form of xides with an oxygen deduction for any ion reported; failure to balance simply ndicates mistakes in calculation. In analyses of ionic minerals reported in terms of ons, failure of the positive and negative ions to balance may occur, and indicates naccuracy of the analysis (lattice defect in the crystal is usually too minute to etect). Analyses of 'atomic' minerals, such as sulphides, rarely balance exactly.

[2] The errors will balance only if both the constituents involved are weighed in the orms they are reported in or have the same conversion factor.

[3] If the several other constituents are denoted by B_pO_q, their molecular weights y b, and the percentages present by y, oxygen will be low if $\Sigma y(n/am - q/bp)$ is ositive.

error as above), while oxygen may be high or low according as this effect or that due to the different oxygen contents of A_mO_n and B_pO_q preponderates (the latter effect makes O high if $am/n < bp/q$). An error of determination (deficit) may make the oxygen ratio high or low, according as the number of oxygen atoms per metal atom in the oxide directly affected, n/m, is less or greater than the mean number in the other oxides; the calculated density also may be high or low, while all other constituents will be high.

If the adopted basis is Σ(O, OH, F) = const., an error of separation will make the calculated density and atomic ratios all high if $am/n < bp/q$, while a deficit in any determination will make the other constituents all high, but the density may be either high or low.

In the above, errors in the separation and determination of the metallic oxides only have been considered. But the determination of some of the anions, particularly fluorine, and the separation of water into hydroxyl and molecular water are especially liable to error. Errors in the determination of hydrate (including zeolitic) water will not affect any of the other constituents unless calculations are made to a basis including the hydrate water, which is unusual. An error by which water which is really present as hydroxyl is accounted as adsorbed water, or lost, will have similar effects to a deficit in a fluorine (or other anion) determination. The effect of a deficit of $x\%$ in fluorine or other anion on the empirical unit-cell contents is to make them all high by half the amount by which F′ is low, (so that Σ(O, OH, F) is low by half the amount that F′ is). In a presentation in atomic ratios to the base Σ(cations) = const., a deficit in fluorine will only affect the oxygen ratio and Σ(O, OH, F), the former being high and the latter low by the factor $(1-x/100)$. If the basis adopted is Σ(O, OH, F) = const., a deficit in F′ leads to high values for all the other constituents, especially oxygen, and normally a high calculated density.[1] If hydroxyl water is accounted as hydrate water, the effects will in general be the same, except that the empirical unit-cell contents will not be affected beyond O″ and OH′, and the calculated densities will be higher than if the water were lost or accounted as adsorbed water.

Errors in the determination of the net state of oxidation of the mineral (commonly a 'ferrous iron' determination)[2] affect the summation, and

[1] The calculated density will be low if the mean equivalent weight of the oxides is less than that of the anion which is in deficit.

[2] It is not always realized that the 'ferrous iron' determination is really no more than a determination of the amount of oxygen necessary to convert all the oxides

ence in a presentation as empirical unit-cell contents, an under-estimation of the degree of oxidation (high value for FeO or V_2O_3, low value for Fe_2O_3 or MnO_2) results in high figures for all the constituents not directly affected. In a presentation to the basis Σ(O, OH, F) = const., under-estimation of the degree of oxidation naturally again results in high values for all the other constituents, while with the basis Σ(cations) = const. the other constituents are unaffected.

In analyses of the kind that are usually reported as ions or atoms a deficit in determination will make all the other ionic ratios high in a presentation as empirical unit-cell contents or as ionic ratios to a basis Σ(ionic charge) = const. An error of separation, in this class of analysis, will involve x% of A being reported as y% of B, since the weighing-forms are rarely the free elements, and any assessment of the effect of such an error must involve the conversion factors for the weighing-forms adopted. If the analysis is a volumetric one, the errors in A and B will often be in the proportion of their equivalent weights; if then the constituent which is in deficit (A) is the heavier, the net sum will be low, and the other ionic ratios will all be high for a presentation as empirical unit-cell contents, but normal for ionic ratios to a basis Σ(ionic charge) = const.

Any discussion of the presentation of chemical analyses would be incomplete without some mention of a method formerly general, as an isomorphous mixture of two or more end-members. For an isomorphous mixture of molecular compounds (for example, hexachlor- and hexabrom-benzene), this method is perfectly suited, but very few minerals are molecular compounds, most being ionic, and in the few that are molecular, the molecule and crystal are often coextensive, as in diamond or quartz. For ionic compounds presentation in terms of isomorphous end-members loses any physical significance, and ceases to be of more than formal value (suited for plotting graphs of correlated physical constants and composition) as soon as variations in both ions occur; in silicates (where in many cases the anion is a chain or net structure coextensive with the crystal, and the term molecule loses all

present to that state of oxidation which is stable under the conditions of the determination. The allocation of the whole of the observed reducing power to FeO, or to $FeO+V_2O_3$, is often purely an arbitrary assumption, necessary because we have no means at present of detecting and determining other lower oxides such as Ti_2O_3, VO_2, or Cu_2O, or higher oxides such as Mn_2O_3 or Co_2O_3, which might conceivably be present. The term 'net state of oxidation' includes, of course, 'available oxygen' determinations in peroxidized minerals such as piedmontite, manganite, or pinium.

force) the necessary postulation of numerous 'end-members', incapable of independent existence and of no structural significance, again reduces this method of presentation to a purely formal one suited only to correlation graphs. The fact that all eight pure end-members of an isomorphous mixture $(NH_4,K)(Al,Fe)[(S,Se)O_4]_2.12H_2O$ are known and stable does not dispose of the fact that a representation of the alum as an isomorphous mixture of four of them is purely formal and of no physical significance; the same applies to the spinels, where most of the end-members are known, and far more forcibly to such a group as the tourmalines where few, if any, of the conceivable 'end-members' are known in anything approaching a pure state. Nor does the fact that the existence of certain silicate molecules in melts is probable necessitate the existence of the same molecules in the solid state.

Summary.

Wherever the necessary data are available with adequate accuracy, the most satisfactory presentation of a chemical analysis is as empirical unit-cell contents, calculated from the cell-sides, density, and chemical data. When empirical unit-cell contents cannot be calculated, some assumption is necessary for a presentation having claims to any structural significance; the assumption to be made should be carefully chosen and explicitly stated. A number of assumptions suitable in special cases are discussed, as is the technique of calculating empirical unit-cell contents, and the effects of errors in the chemical analysis on the several forms of presentation.

The 'baddelyite from Alnö'—an error.

By H. von Eckermann, Ph.D., F.G.S.

[Read June 8, 1939]

IN most mineralogical text-books the nepheline-syenite area of Alnö, on the east coast of Sweden, is given as one of the few localities of the rare mineral baddelyite, ZrO_2. This information is based on a communication by E. Hussak,[1] who claimed to have discovered the mineral in jacupirangitic varieties of the Alnö nepheline-syenites.

The present writer, being engaged with a petrological and mineralogical revision of the Alnö occurrence, earlier described by A. G. Högbom[2] in his classic memoir of 1895, has in vain looked for the presence of baddelyite. Hussak claimed to have isolated by means of Klein's solution 0·38 gram of pure baddelyite from 100 grams of rock, as well as to have obtained characteristic ZrO_2 crystals in a borax bead test. Repeated isolation tests with Clerici's solution on samples from various localities within the Alnö area, however, furnished nothing but residues of melanitic garnet.

If a percentage of close to 0·4 ZrO_2 were really present in the rock, the prominent Swedish chemists Sahlbom, Blix, and Berggren, collaborating with the present writer, could hardly have failed to detect it. Numerous analyses and spectrograms of the jacupirangitic rocks of Alnö have been executed without disclosing even traces of ZrO_2. On the whole, zirconium has been found to be an extremely rare element in the nepheline-syenites of the region. After having examined hundreds of thin sections the present writer, therefore, has come to the conclusion that the mineral baddelyite probably does not exist at Alnö, and certainly not in the mineral paragenesis, claimed by Hussak, whose assertion to the contrary must be founded on error.

As a reasonable explanation of his mistake may be suggested the confusion with anisotropic, highly titaniferous melanite. This latter mineral occurs interstitially within the fabric of the jacupirangitic differentiates of Alnö; the typical garnet crystal-form being suppressed or distorted. Besides, the garnet is occasionally found to be zonal in a way that may easily be mistaken for the twinning on (100) or (110) of baddelyite.

[1] E. Hussak, Neues Jahrb. Min., 1898, vol. ii, pp. 228–229.

[2] A. G. Högbom, Geol. För. Förh. Stockholm, 1895, vol. 17, pp. 100–158, 214–248.

The optical characteristic values of the highest birefringent melanite were determined by the present writer and are given below in comparison with those of baddelyite, as recorded by Larsen.

	Anomalously birefringent Alnö melanite.	Baddelyite.
2V (Na) ...	24°–33° (negative)	2V ... 30° (negative)
β	1·91–1·98	β ... 2·19
$\gamma-\alpha$ (Na)...	0·042–0·056	$\gamma-\alpha$ ... 0·070

This striking agreement between the optical values may have led Hussak to his erroneous conclusion, especially as he carried out his investigations on a few samples of dunitic jacupirangite, supplied by Högbom, without being familiar with the aspect of birefringent 'dodecahedral' melanite, generally occurring in most other types of Alnö nepheline-syenites. A check by the present writer on Högbom's original material, still preserved, failed to disclose the presence of any baddelyite. Hussak may also have been influenced by the suggestive similarity in the mineral paragenesis of the basic varieties of the Brazilian and the Alnö jacupirangites.

Hussak's measurement of crystal angles corresponding with those of baddelyite is puzzling, as also is his statement of an 'oil-green to reddish-brown' pleochroism. The former may be due to a mix-up with Brazilian crystals in his laboratory; and the latter suggests a confusion with titaniferous pyroxene. On the other hand, there is a slight possibility of the samples, sent by Högbom, being exceptional boulders picked up along the Alnö shore and derived from another alkalic locality. Such an occurrence has recently been discovered by the present writer about 18 miles north of Alnö, where it lies submerged. The adjoining shores of the Baltic are littered with carbonatitic boulders.

However this may be, the present writer can but conclude that the present references in the mineralogical text-books to Alnö as a locality for baddelyite are erroneous.

Crystal-structure of a natural nickel-iron alloy.

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University College of North Wales, Bangor.

[Read June 8, 1939; communicated by the editor.]

1. *Introduction.*

NATURAL nickel-iron alloys have been found in several places on the earth's surface. In addition to alloys containing a low percentage of nickel (about 3%), there are others which contain much higher percentages of nickel (about 70%). To alloys of the latter group the name awaruite is now generally given and it may include josephinite, souesite, and other alloys possessing high nickel content so long as they belong to the same phase and possess identical crystal-structures.

It is of interest to the mineralogist to know whether these alloys conform to the structure of nickel-iron alloys prepared in the laboratory and whether they fit into the accepted phase diagram of the nickel-iron system. It is of interest also to the physicist and the metallurgist to obtain information concerning these natural alloys, because some nickel-iron alloys made in the laboratory are difficult to prepare in a state of true equilibrium. Data derived from the study of the natural alloys may help to throw light upon the structure of these artificial alloys.

2. *Previous Work on Natural Nickel-iron Alloys.*

Several investigations of natural nickel-iron alloys have been described. W. H. Melville[1] records the examination of magnetic pebbles discovered in large quantities in the gravel of a stream in Josephine and Jackson Counties in Oregon. The pebbles had smooth surfaces, coloured greenish-black and interrupted by slight areas of greyish-white alloy of nickel and iron. Upon analysis this alloy was found to contain 23·22% of iron and 60·45% of nickel by weight, which, the author points out, corresponds with the formula Fe_2Ni_5. The name josephinite was given to the material.

Another investigation on pebbles of 'josephinite' from Josephine County was carried out by G. S. Jamieson,[2] who found the alloy to be of a spongy nature, binding together and enclosing particles of serpentine.

[1] W. H. Melville, Amer. Journ. Sci., 1892, ser. 3, vol. 43, p. 509.

[2] G. S. Jamieson, ibid., 1905, ser. 4, vol. 19, p. 413.

The material on analysis yielded 25·24% of iron and 74·17% of nickel, with other elements, the chief of which was cobalt.

Souesite, a mineral containing 22·02% of iron and 75·50% of nickel, found in British Columbia, was examined by G. C. Hoffmann.[1] The nickel-iron alloy in this mineral was found in the form of small very irregularly shaped, rounded grains (maximum diameter about 1·5 mm.) of a faint yellowish steel-grey colour. It was malleable and strongly magnetic.

The original 'awaruite' from New Zealand examined by W. Skey in 1885 contained 31·02% of iron, 67·63% of nickel, and 0·70% of cobalt. The ratio of the number of nickel to the number of iron atoms in each of these minerals is given in the following table.

Mineral.	Atomic ratio (Ni/Fe).
Awaruite, New Zealand (Skey)	2·07
Josephinite, Oregon (Melville)	2·48
Josephinite, Oregon (Jamieson) ...	2·80
Souesite, British Columbia (Hoffmann)	3·26

Jamieson suggested that since all the minerals seemed to exhibit a certain uniformity of composition, the name 'awaruite' should alone be used for these terrestrial nickel-iron alloys, rich in nickel, even though there was no evidence that a definite compound of nickel and iron existed.

3. *Material.*

The material used in the present investigation was received from Dr. Fletcher Watson of Harvard College Observatory, Cambridge, Massachusetts, through the kindness of Professor Charles Palache of the Department of Mineralogy, Harvard University. It is recorded in Harvard Museum as being awaruite from Grant's Pass, Josephine County, Oregon, U.S.A., the Harvard number being 81,539. It was stated to contain between 70 and 75% by weight of nickel.

The sample received for examination weighed about 13 grams and was of a prolate spheroidal shape, the major axis measuring about 20 mm., and the minor axis about 14 mm. Its outer surface was covered with a smooth vitreous layer and was in places dented. When scratched with a file it showed metallic lustre. The material was somewhat brittle, but on filing it yielded a fine powder which was dark in colour owing probably to the presence of impurity, which will be assumed to consist mainly of serpentine. It was difficult to prepare a surface satisfactorily polished on account of the hardness of the material. A carefully prepared surface when examined under moderately high power showed the

[1] G. C. Hoffmann Amer. Journ. Sci., 1905, ser. 4, vol. 19, p. 319.

existence of a large number of fine cracks together with a few of larger size.

4. *Occluded Gases.*

Part of the technique in preparing powder for X-ray examination is to heat the powder gently in a tube connected directly to a pump capable of maintaining a vacuum of about 0·001 mm. of mercury. During this operation it was discovered that a comparatively large quantity of gas was discharged by the material, the gas being emitted in bursts, as seen by the disturbance of the powder which at intervals was greatly agitated by the expulsion of the gas.

A careful analysis of the gas emitted was conducted by Professor W. M. Travers of Bristol University, to whom we are greatly indebted. The weight of specimen used for this purpose was 1·5 gm. It yielded 1·5 c.c. of gas which consisted of hydrogen and carbon monoxide in equal proportions, the amount of the residual gas, the nature of which is unknown, being less than 0·05 c.c. The density of the alloy, the measurement of which is referred to below, was found to be 6·6 gm. per c.c., so that the volume of 1·5 gm. is approximately 0·25 c.c. The material therefore yields at least 30 times its own volume of gas, half of which is hydrogen and half carbon monoxide. Hydrogen mainly was displaced at the start, but on prolonging the heating more carbon monoxide was evolved.

As the temperature of a specimen of the material in powder form was raised from room-temperature to about 900° C., gas was discharged at all temperatures. The average rate of discharge was slow at first, increasing to a maximum at about 400° C.

5. *Density.*

Owing to the presence of occluded gases, and the small amount of material available, difficulty was experienced in making an accurate determination of and in reaching finality concerning the density of the material. Many observations were made with material both in lump and in powder form, in the degassed and in the original condition, by weighing in water in some cases and in paraffin oil in others. The following gives a summary of the determinations made of the density.

Condition of Material.	Density gm. per c.c.
(1) Original lump, without any treatment	6·58
(2) Portion of lump, after being degassed	6·65
(3) Powder, after being degassed ...	6·70

Taking into account that the original lump under (1) was of greater mass than the degassed portion under (2), and that not a great quantity of powder was available for the determinations under (3), the value of the density was taken to be 6·6 gm. per c.c. This value is very much lower than the density (8·5 gm. per c.c.) of an artificially prepared alloy of the same nickel content.

6. *X-ray examination.*

For the X-ray examination a small quantity of filings was taken, the filings having passed through a sieve of 100 mesh. The powder specimens were mounted on a glass fibre which was rotated at the centre of a circular camera, along a diameter of which a beam of X-rays was passed. The beam fell on the powder specimen, and on the photographic film a spectrum was obtained which was characteristic of a face-centred cubic structure. The specimens examined were submitted to various treatments before irradiation. The spectra reproduced in fig. 1 were obtained with powder specimens which were in the following conditions: (1) specimen not submitted to any treatment; (2) specimen partly degassed by heating gently while in vacuo for about fifteen minutes; (3) specimen given the same treatment as (2) but afterwards annealed at 300° C. for seven days; (4) specimen thoroughly degassed and annealed at 300° C. for seven days; (5) specimen not degassed but annealed for two weeks at 300° C.; (6) specimen thoroughly degassed and annealed for two weeks at 300° C. Spectra (1) to (4) were obtained with cobalt and (5) and (6) with iron radiation. In each case the specimen was allowed to cool in the furnace after the annealing treatment. It cooled from 300° C. to room-temperature in about three hours.

These six spectra yield parameters that are identical within the accuracy of measurement, but the width of the lines progressively decreased from (1) to (4), which is to be expected, as the distortion produced by the cold-work done in preparing the filings will be gradually removed by the heat-treatment. The removal of the gas occluded in the specimen also improves the definition of the lines, as will be observed by comparing spectra (1) and (2). The material, however, is still in a distorted condition even after the heat-treatment given to it under (4) or (6). It is accentuated in (6) owing to the more open spectrum obtained with iron radiation.

The work on artificial nickel-iron alloys in the region of composition 70 atomic % nickel, has shown that spectra characteristic of a face-centred cubic structure are obtained whatever the temperature of anneal-

g. This is the case with alloys in a pure phase. It was therefore ecided, in view of the distorted condition in which the specimens were und after the heat-treatment already mentioned, to submit samples the material to annealing treatments at higher temperatures and for

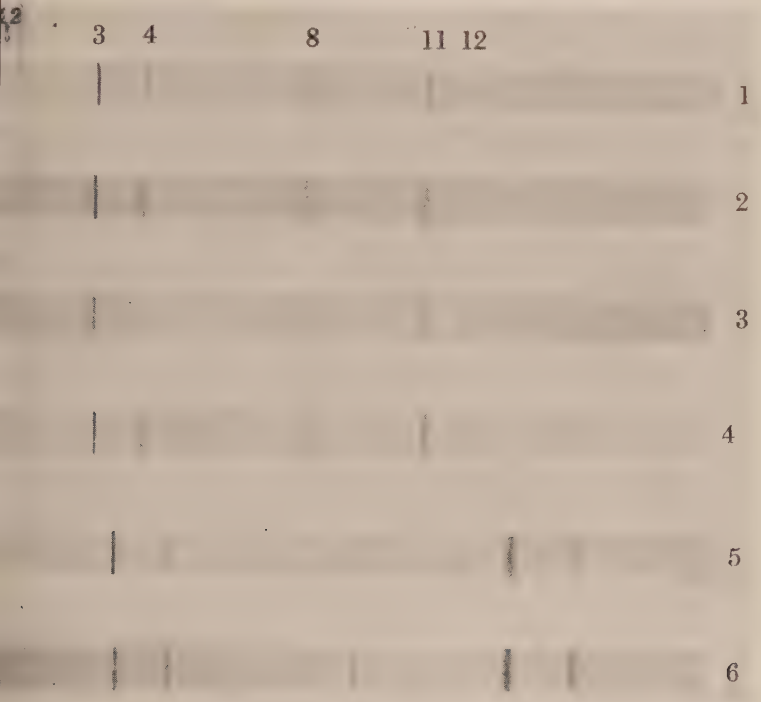

FIG. 1. X-ray powder photographs of nickel-iron alloy.

nger periods. The spectra reproduced in fig. 2 were obtained with wder specimens which had been given the following treatments:) annealed for eight days at 500° C. and air cooled, cobalt radiation th iron filter; (2) same treatment, but spectrum obtained with iron diation and manganese filter; (3) same treatment as (1) and (2) llowed by an additional three weeks annealing at 350° C. and air oled, cobalt radiation with iron filter; (4) specimen of pure nickel-iron oy containing 73% by weight of nickel, annealed for five months at 0° C., cobalt radiation with iron filter. The iron filter is not essential nen irradiating a nickel-iron alloy with cobalt radiation, but with it e background is improved.

The lines in this series of spectra are well defined, showing that the material after the heat-treatment, to which it was submitted, had lost most of the distortion which existed after the first heat-treatment. Spectrum (2) was taken with iron radiation for greater accuracy in measurement and also as a check on spectrum (1) in which faint lines were to be observed. These lines were found also in the second spectrum, and will be referred to later. The longer annealing given to the specimen

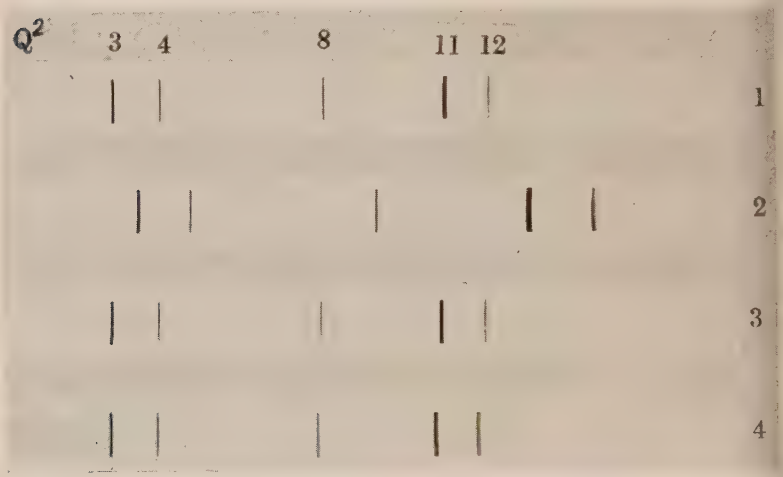

Fig. 2. X-ray powder photographs of nickel-iron alloy.

which yielded spectrum (3) with cobalt radiation shows the reflection from the (222) plane to be almost resolved into its components α_1 and α_2. The resolution of the doublet is complete in the reflection from this plane in the spectrum of the artificial alloy. All the spectra are identical in that they indicate the presence of a face-centred cubic structure, and the parameter of the alloy in awaruite, as far as can be judged from the spectra, is the same after each heat-treatment. All the spectra containing well-defined lines contained faint lines in addition to the normal set of lines from the face-centred cubic lattice. No additional lines were observed in the spectrum of the artificial alloy (4, fig. 2).

To arrive at an accurate value of the parameter of the crystal lattice other photographs were taken with a focusing camera, with which it was possible to obtain lines at very large angles of reflection. The mean of several determinations gave 3·5516Å. for the parameter of the natural alloy at 15° C.

7. *Chemical Analysis.*

It was decided at this stage to submit the material to careful chemical analysis to ascertain the exact amount of iron present in relation to the amount of nickel, also the total amount of impurity. Analyses were carried out on two separate samples by Mr. R. Johnston of the Midland Laboratory Guild (1928) Ltd., Birmingham, who reports:

"The mineral was dissolved in a mixture of three parts of hydrochloric acid and one of nitric acid, and when it was so far dissolved that all action appeared to have ceased the assay was evaporated on a water-bath to dryness, and then baked well. It was then taken up with dilute hydrochloric acid, and the insoluble residue filtered off and kept (Residue 'A').

"The filtrate was treated with hydrogen sulphide and any resulting precipitate filtered off. The liquid was boiled free from the gas, oxidized, and made up to an exact bulk. Aliquot portions of this bulk were measured off for the assays of nickel and iron.

"The portions for iron were precipitated with ammonia and the ferric hydroxide filtered off and dissolved in hydrochloric acid, reduced in the cold with hydrogen sulphide, boiled free, cooled and titrated with potassium dichromate using diphenyl amine as internal indicator.

"The nickel portions were evaporated to about 5 c.c. and 5 gm. of solid ammonium chloride added to each. Then the iron was precipitated with 50 per cent. ammonia and filtered off, and washed with dilute ammonia water containing ammonium chloride. The iron hydroxide was redissolved, evaporated, and treated as before, and precipitated again, the filtrates being added together. This triple precipitation was carried out to ensure that all the nickel was freed from the iron. The faintly ammoniacal nickel solution was warmed to about 70° C. and the nickel precipitated with alcoholic dimethylglyoxime and digested for one hour. The oxime filtered on to a Gooch crucible, washed, and dried at 120° C. and weighed when cool.

"Residue 'A' was weighed, and then fused with potassium bisulphate and leached out with dilute sulphuric acid. The unaffected residue was filtered off and washed, and the iron in the filtrate determined as before by titration. The resulting iron was added to the total. The final insoluble residue was white, and we assumed that this was silica or the like, and not carrying any iron. However, fusion with soda would be needed to be absolutely sure of this, though it is hard to suppose that iron could withstand the action of fused bisulphate at a red heat.

"In view of the small amount of sample available, the accuracy of the method could be $\pm 0{\cdot}05\%$ for the nickel, and $\pm 0{\cdot}10\%$ for the iron. Probably the results are well within these limits."

The first sample submitted for analysis was a lump of the original specimen weighing 1·8248 gm., about half the surface of which was covered with a layer of vitreous material (this being the outer surface of the original specimen) and the remainder of the surface was freshly cut. The analysis showed that the absolute percentages were as follows by weight:

Iron	$26{\cdot}90 \pm 0{\cdot}10\%$	atomic ratio Ni/Fe = 2·01
Nickel	$57{\cdot}25 \pm 0{\cdot}05\%$	
Impurities ...	15·85 (by difference).	

After solution in acids there was filtered off a dark red powdery residue. With 1·8248 gm. of specimen this residue weighed 0·2304 gm. or 12·6% of the original weight. This was then fused with potassium bisulphate ($KHSO_4$) and leached out. The iron thus recovered amounted to 0·1178 gm. or 6·46% of the original weight of the specimen. This is included in the iron content given in the above analysis. It is possible that some of the iron found in the insoluble residue may not be alloyed.

In order to arrive at more definite results, another sample was submitted for analysis. The vitreous layer was removed and the material thoroughly degassed before commencing the analysis. This sample yielded the following absolute percentages:

Iron ... ... $26{\cdot}50_6 \pm 0{\cdot}10\%$
Nickel ... ... $60{\cdot}42 \pm 0{\cdot}05\%$
} atomic ratio Ni/Fe = 2·16
Impurities ... $13{\cdot}07_4$ (by difference).

With this sample the insoluble residue after treatment with acids amounted to 3·30% of the original weight. This on fusion with potassium bisulphate yielded 0·056% of iron, which is included in the iron content (26·506) given in the above analysis.

There is a marked difference between the amount of iron recovered from the insoluble residue in the two cases. Also the amount of insoluble residue is very different. Since there is such a small amount of residue found in the second sample compared with the first, the figures of the second analysis have been taken as representing the composition of the interior of the specimen more accurately than those of the first analysis, and will be used in calculations that may follow.

8. *Discussion.*

It has been mentioned that on careful examination the spectra in fig. 2 contain lines in addition to those characteristic of a face-centred cubic structure for which the values of $Q^2 [= (h^2+k^2+l^2)]$ for the first five lines are 3, 4, 8, 11, and 12. The faint lines were measured and it was found that three fitted the values of $Q^2 = 2$, 5, and 6, but the remaining three did not fit, although they fell near the lines of a simple cube. This suggested a super-lattice, and the point was further investigated.

It was assumed that in each elementary cell there was an atom of oxygen in addition to two atoms of nickel and one atom of iron. Such an assumption might cover the possibility that the alloy dissolved a certain amount of nickel oxide. The suggestion can be checked by calculation of the amount of impurity (assuming it to be mainly serpentine

density 2·6 gm. per c.c.) in relation to the amount of alloy. The nsity of the alloy constituted as above works out to be 7·0 gm. per c.c. the lattice parameter is taken to be 3·5516Å. and the atomic weights oxygen, iron, and nickel are taken to be 16·0, 55·84, and 58·69 respec-vely. Taking the density of the original material to be 6·6 gm. per c.c., e ratio of the volume of alloy to the volume of impurity is found to be or the ratio of the masses is 27. But from the chemical analysis the tio of their masses is 86·926/13·074 = 6·65. The disagreement between ese figures is so great that it invalidates the assumption that the super-ttice mentioned exists in the material. The extra lines observed in the ectra must therefore be put down to impurities.

It will next be assumed that the material consists of pure nickel-iron loy mixed with impurities. Taking the figures from the analysis, and suming that all the iron and nickel present alloy with each other, then ere is present in the alloy 30·49% of iron and 69·51% of nickel by ight, that is, 31·6 atoms of iron to 68·4 atoms of nickel. The ratio of e number of nickel atoms to iron atoms is therefore 2·16.

If the iron found in the insoluble residue (0·056%) be omitted, the omic ratio Ni:Fe becomes 2·12, which is not appreciably different om the other value. Whichever figure is taken, the ratio agrees tter with the formula $FeNi_2$ than with the formula Fe_2Ni_5.

Calculating again, as was done previously, the ratio of the mass of pure loy to the mass of the impurities, but in this case taking the density of e alloy to be 8·5 grams per c.c. (calculated on the basis of the para-eter value 3·5516Å. and a ratio of two atoms of nickel to one of iron), becomes 6·5 against 6·6 found by chemical analysis. The agreement re is remarkably good, and lends support to the view that the material nsists of a mixture of nickel-iron alloy and an impurity which is sumed to be serpentine.

Another view may be put forward. If it be assumed that the natural loy consists only of iron and nickel with no impurities entering the ttice, then from the parameter-composition curve[1] obtained with alloys tificially prepared from pure nickel and iron, a parameter of 3·5516Å. rresponds with a composition of 70·9 atomic % nickel, which makes e atomic ratio Ni:Fe = 2·44. This figure is nearer 2·5 than 2·0, agree-g more closely with the formula Fe_2Ni_5 than with the formula $FeNi_2$. There is no direct means of deciding definitely between these two ntradictory results. The assumption that no impurity enters the

[1] See E. A. Owen, E. L. Yates, and A. H. Sully, Proc. Physical Soc., 1937, vol. 49, 315.

lattice of the natural alloy is, however, unlikely to be true, especially as cobalt and copper are usually found in small quantities in these minerals. The lattice parameter of a pure nickel-iron alloy containing 68·4 atomic % nickel is 3·5550Å. The lattice parameter of the natural alloy (3·5516Å.) is therefore slightly smaller than that of an artificial alloy of the same composition; the difference in parameter is 0·0034Å., corresponding to a difference in density of about $0·02_5$ or 0·3%. A slight amount of impurity, if it entered the lattice, might account for this difference. It is probably safer in this instance to accept the conclusions reached from chemical analysis than from measurements of lattice parameter, although neither course is free from objection.

9. *Conclusions.*

(1) The mineral 'awaruite' from Grant's Pass, Josephine County, Oregon, consists of a mixture of nickel-iron alloy with impurities, the chief of which is probably serpentine.

(2) Chemical analysis shows the mineral to contain 26·50% of iron, 60·42% of nickel, and 13·07% of impurity. (Deducting impurities, 30·49% Fe, 69·51% Ni.) The ratio of the number of nickel to the number of iron atoms present in the mineral is 2·16.

(3) This mineral has a density of 6·6 grams per c.c., the density of the nickel-iron alloy alone being 8·5 grams per c.c.

(4) The mineral contains thirty times its own volume of gas made up of a mixture of hydrogen and carbon monoxide in equal proportions. The gas is discharged at all temperatures up to 900° C., but the rate of discharge reaches a maximum at about 400° C.

(5) The nickel-iron alloy possesses a face-centred cubic structure, the lattice parameter of which is 3·5516Å. The lattice parameter of an artificially prepared alloy of the same composition is 3·5550Å.

(6) The investigation does not definitely decide whether the alloy conforms to the formula $FeNi_2$ or to the formula Fe_2Ni_5. Certain considerations point to the former as being the more probable.

10. *Acknowledgements.*

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